

ANALYTICAL ABSTRACTS



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ANALYTICAL ABSTRACTS

1.—GENERAL ANALYTICAL CHEMISTRY

1736. Use and abuse of pH measurements. I. Feldman (The Univ., Rochester, N. Y., U.S.A.). *Anal. Chem.*, 1956, **28** (12), 1859-1866.—Following a review of the development of the concept of pH, the liquid-junction potential problem arising from the use of the pH meter is discussed, with special reference to the probable extent of the error in pH measurements in aq. soln. In certain relatively simple conditions there is an approx. relation between the pH-meter reading and the $[H^+]$, otherwise the reading is only a reproducible reference point without theoretical significance, or is not even that. Examples of such instances are given, and the practical interpretation of pH measurements in aq. and non-aq. soln., colloids and suspensions is discussed. Various pH scales are described and compared.

W. J. BAKER

1737. Removal of ethanol from chloroform. G. Wohlleben (Chem. Lab., Firma M. Woelm, Eschwege, Germany). *Angew. Chem.*, 1956, **68** (23), 752-753.—The new process described for the preparation of $CHCl_3$ that is free from stabilisers is based on adsorptive filtration on highly activated alumina. *Procedure*—Filter a maximum vol. of 550 ml of $CHCl_3$ through a column (37 mm in diam.) containing 250 g of alumina. At normal filtration rate (0.7 hr. for 550 ml), and collecting the fraction from 200 to 500 ml, a max. ethanol content of 0.01% is obtained. By restricting the flow rate to 6-5 hr. for 550 ml, and collecting the $CHCl_3$ fraction from 150 to 500 ml, the ethanol content is reduced to a max. of 0.005%. Traces of water and acid are also removed. The method of Bryant *et al.* (*J. Amer. Chem. Soc.*, 1940, **62**, 1) is recommended for the determination of ethanol in $CHCl_3$.

D. F. PHILLIPS

1738. Qualitative analysis of cations with the aid of metal indicators. W. Berger and H. Elvers (Lab. VALVO G.m.b.H., Radioröhrenfabrik, Hamburg). *Z. anal. Chem.*, 1957, **154** (2), 114-121.—A scheme of micro-analysis, based on the use of metal indicators, such as Eriochrome black T, and the formation of complexes, has been developed. Special microchemical apparatus is not necessary and the method can be semi-quantitative.

M. F. C. LADD

1739. Co-precipitation in quantitative analysis. IV. Study of zinc mercury thiocyanate as a collector. A. K. Babko and S. V. Radzikovskaya (Kiev State Univ.). *Zavod. Lab.*, 1956, **22** (11), 1271-1276.—The molar solubilities of the mercury thiocyanates of Zn, Cu and Co at 18° to 20° are 1.4×10^{-4} , 2.7×10^{-4} and 4.8×10^{-4} , respectively. Co-pptn. of Cu, Co and other metals with Zn occurs at concn. well below that of the corresponding salt. In the presence of ten times as much Zn, co-pptn.

of Cu and Co is almost complete. Increase in the concn. of Zn improves the co-pptn. if excess of mercury thiocyanate ions is present. Co-pptn. is due to the formation of solid soln., but the degree of co-pptn. depends little on the radius of the cation and is mainly a question of relative solubilities.

G. S. SMITH

1740. Use of hydrochloric acid solution of iodine trichloride in volumetric analysis. III. F. E. Kagan (Kiev Postgrad. Med. Inst.). *Ukrain. Khim. Zhur.*, 1956, **22** (1), 94-96.—An aq. soln. ($\approx 0.1N$) (5 ml) of a phenol or an aromatic amine is diluted with 150 to 200 ml of water at 60° to 70°, 25 to 30 ml of 0.1 N ICl_3 is added, and the soln. is shaken for 30 min. (for resorcinol ≈ 3 min.). Aq. KI (10%) (10 ml) is then added and the iodine liberated in the reaction (substance + $xICl_3 \rightarrow x$ -iodo deriv. + $xHCl$ + xCl_2) is titrated with 0.1 N $Na_2S_2O_3$. The values of x for a number of substances are—anisole, 1; *p*-chloro- and *p*-nitro-phenol, thymol, hexyl-resorcinol, Na *p*-aminosalicylate, *o*- and *p*-toluidine, and procaine, 2; resorcinol and aniline, 3; and 2-hydroxyquinoline and 3:4-di-(*p*-hydroxyphenyl)-hexane, 4.

R. TRUSCOE

1741. Analysis for industry [uses of ascorbic acid as a reducing titrant]. A. McDonald. *Ind. Chem. Mfr.*, 1956, **32**, 545-547.—A review of the literature for the past five years is presented. (24 references.) S.C.I. ABSTR.

1742. Compleximetric titrations (chelatology). XXIII. Xylenol orange, a new specific indicator. J. Körbl, R. Pribil and A. Emr (Res. Inst. Pharm. Biochem., Prague, Czechoslovakia). *Chem. Listy*, 1956, **50** (9), 1440-1444.—The colour reactions of [6-di(carboxymethyl)aminomethyl-*o*-cresol]sulphonephthalein (xylenol orange) (I) with various elements were studied. I has been found to be an excellent indicator for compleximetric titrations of Bi^{3+} , Th^{4+} , Sc^{3+} , La^{3+} , Pb^{2+} , Zn^{2+} and Cd^{2+} in acid soln. At the equivalence point, the colour of the indicator changes very sharply from intense red to yellow. The following media are suitable for the compleximetric titrations—for Bi, HNO_3 (pH 1 to 3); Th, buffer soln. pH 3; Sc, buffer soln. pH 5; La, Pb and Zn, buffer soln. pH 5, or hexamine; Cd, hexamine soln. with one drop of pyridine. A mixture of acetic acid and Na acetate has been used as buffer soln. and a 0.1% aq. soln. of I as indicator. The titrations of Cr^{3+} , Cu^{2+} , Hg^{2+} , Fe^{3+} and Al^{3+} , with the same indicator, were also studied. The reaction of I with Al^{3+} seems to be of value for the detection of Al. In all the titrations mentioned, Fe^{3+} must first be reduced. J. ZÝKA

1743. Conductimetric titrations in chelatology. I. Introduction. F. Vydra and M. Karlik (Vysoká škola chem.-technol., Prague, Czechoslovakia). *Chem. Listy*, 1956, **50** (11), 1749-1753.—The conductimetric titration of some metals with 0.02 M soln. of EDTA (disodium salt) (I) or of the disodium

salt of 1:2-diaminocyclohexane-NNN'-tetra-acetic acid (II) was studied. All titrations were carried out in a vol. of 200 ml, redistilled water being used. Satisfactory results were obtained by titrating Ni, Cu, Pb, Co, Zn, Hg and Mn in slightly acid (pH 5 to 6) unbuffered medium, with II as titrant. The titration of Ca, Sr, Ba, Zn, Cu, Ni, Co, Mn and Cd can be carried out in 0.005 to 0.1 M aq. NH_3 with the same volumetric reagent, and that of Ca, Ba, Sr and Mg with I and II in Sørensen borate buffer soln. The titration of Zn, Cd, Ni and Co in slightly acid soln. (acetate buffer) yields good results. Small amounts of Ca can be titrated at pH 8 (ammonium acetate-acetic acid) with I; under these conditions Mg does not react. The results were in good agreement with those from visual chelatometric and gravimetric determinations. The described method is recommended for semi-micro and micro-analytical purposes. J. ŽYKA

1744. Use of organic sulphur derivatives in volumetric analysis. II. Potassium mercaptophenylthiadiazolone as titrant. J. Čihálik and J. Voráček (Inst. Anal. Chem., Charles' Univ., Prague, Czechoslovakia). *Chem. Listy*, 1956, 50 (11), 1780-1785.—The polarographic behaviour of bismuthon (5-mercapto-3-phenyl-2-thio-1:3:4-thiadiazol-2-one) (I) was studied. Suitable conditions have been found for the polarographic titration of Ag^+ , Hg^{2+} and Pb^{2+} . An aq. or ethanolic soln. (0.05 M) of I was used as titrant, its standardisation being effected by potentiometric argentimetric titration. The soln. must be stored in an atmosphere of N, and checked weekly. From 5 to 15 mg of Ag^+ can be titrated in 15 ml of soln. (pH 1 to 6) containing 3 ml of 1 M KNO_3 (e.m.f. -0.7 V), with a range of error of $\pm 0.13\%$. EDTA does not interfere. The titration of Pb should be carried out at pH 5 to 7, in 15 to 30 ml of soln. containing 0.2 M KNO_3 (e.m.f. -0.89 V). In the determination of about 10 mg of Pb, the error was not greater than $\pm 0.47\%$. Univalent Hg can be titrated at pH 1 to 6; KNO_3 must be present (e.m.f. -0.70 V). The range of error for 3 to 50 mg of Hg is $\pm 0.32\%$. The potentiometric determination of 5 to 15 mg of Hg^{2+} (pH 3 to 6) gives good results; the error is within ± 0.24 . In the polarographic titrations the system used was the dropping-mercury electrode - S.C.E. J. ŽYKA

1745. Coulometry. E. H. Swift (California Inst. of Technol., Pasadena, U.S.A.). *Anal. Chem.*, 1956, 28 (12), 1804-1806.—A short review is given of the development, principles and applications of coulometry. (7 references.) K. A. PROCTOR

1746. Flame photometry. V. W. Meloché (Dept. of Chem., Univ. of Wisconsin, Madison, U.S.A.). *Anal. Chem.*, 1956, 28 (12), 1844-1847.—This review includes sections on early methods, instruments, atomisers and burners, flame-temp. effects, interferences and special instrumentation. (58 references.) K. A. PROCTOR

1747. Notes on the literature of spectral analysis. I. The spectrum of iron in Brode's tables. J. Knop (Chem. Inst., Vysoká škola zemědělská, Brno, Czechoslovakia). *Chem. Listy*, 1956, 50 (12), 2040-2041.—Some errors in the values of wavelengths in Brode's spectrum of Fe were corrected by a comparison with various spectral tables as well as by exact measurement. A list of values is included. J. ŽYKA

1748. Accuracy of photographic methods of spectrographic analysis. V. L. Ginzburg, E. F. Alekseenko, E. E. Belokrinskaya, I. N. Vitushkina and F. M. Ineshina (Norilsk Mining Metall. Combine). *Zavod. Lab.*, 1956, 22 (11), 1331-1333.—From the results of many readings the use of a fixed calibration curve is found to give smaller errors than does the three-standard method. G. S. SMITH

1749. Investigations of the influence of third constituents on spectrochemical analysis. J. van Calker and R. Wienecke (Univ. Münster, Germany). *Forschungsber. Wirtschafts- u. Verkehrsministeriums Nordrhein-Westfalen*, 1955, No. 141, 25 pp.—The concn. ratio of two elements is readily determined from a working curve showing photographic blackening of spectral lines as a function of concn. The spectrochemical analysis may be in error by the presence of a third element because of changes in the mechanism of the discharge, chemical reactions, or direct effect on the spectral excitation processes in the light source. Spectrochemical buffers can be employed to stabilise the discharge and a carbon counter electrode suppresses oxidation reactions in the spark gap. Excitation functions and intensity-time curves of spectral lines in sparks show that a third element affects the light emission of other elements. These phenomena are illustrated by the spectrochemical determination of Mg in aluminium when Zn is also present. CHEM. ABSTR.

1750. Effect of third components [in spectrographic analysis]. I. A. Kovalev (Kharkov Filial Niikhim-mash). *Zavod. Lab.*, 1956, 22 (11), 1336-1337.—Calibration curves based on the formula derived earlier (*Anal. Abstr.*, 1956, 3, 3794) are not displaced by a third component. Thus the determinations of Na and K are not affected by the addition of Ca or Al. G. S. SMITH

1751. Use of chemical reactions in the processes of spectrographic analysis. N. F. Zakhariya, N. A. Fuga and Ts. A. Leiderman. *Zavod. Lab.*, 1956, 22 (11), 1303-1306.—The use of halogenation reactions is described. To analyse aluminosilicates, the sample (1 pt.) is mixed with a mixture (4 pt.) of CaCO_3 (8 pt.) and NH_4Cl (1 pt.) and formed into a briquette (50 to 100 mg) which is volatilised in an arc. The alkali metals form chlorides which volatilise quickly and completely. The sensitivity of the determination of Li, Cs and Rb by means of the arc is increased. The results are not affected by the other elements present, apart from Na and K. It is advisable to add the same amount of KNaCO_3 (2 to 3%) both to the sample and the standards, which can be based on quartz. To determine In and Tl in sulphide ores and minerals, the samples are first ignited to give the oxides, which are then briquetted with AgI and excited in the arc. To determine small amounts of impurities in W, Hf, Mo, etc., some success has been obtained by the addition of PbCl_2 , CuCl_2 , CuCl or AgCl (in order of increasing activity). G. S. SMITH

1752. Effect of current strength on the slope of [spectrographic] calibration curves. Yu. Ya. Kolbovskii and M. K. Krizhanovskaya (Yuzhnorub Metall. Works). *Zavod. Lab.*, 1956, 22 (11), 1334-1335.—With arc excitation, errors are least when high currents (>6 amp.) are used with the fixed calibration curve method, and when low currents are used with the three-standard method. G. S. SMITH

1753. **New methods of polarographic analysis.** Z. Zagórski. *Chem. Anal., Warsaw*, 1956, **1** (2-3), 3-14.—An extensive survey is presented of the latest developments in polarographic analysis, with special reference to testing inorganic materials. Oscillopolarography is considered to be of special value for the continuous chemical control of reactors, liquids in pipe-lines, pharmaceuticals and air in industrial establishments. (47 references.)

K. F. SPOREK

1754. **Thermogravimetry and its use in analytical chemistry.** Z. F. Shakhova and E. N. Semenovskaya. *Zavod. Lab.*, 1956, **22** (12), 1430-1435.—A review with 55 references.

G. S. SMITH

1755. **Chemical analysis by electron diffraction.** Shigeto Yamaguchi (Scientific Res. Inst. Ltd., Hongo, Tokyo, Japan). *Z. anal. Chem.*, 1957, **154** (1), 28-31.—Chemical analysis by electron diffraction is considered with reference to simple inorganic mixtures such as ThO_2 -MgO and ThO_2 -NaF.

M. F. C. LADD

1756. **The investigation of various chemical systems by electron-spin resonance.** D. J. E. Ingram (Dept. of Electronics, Univ. of Southampton, England). *Analyst*, 1956, **81**, 681-687.—An outline is given of the applications of electron-resonance techniques beyond the measurement of small quantities of paramagnetic atoms. Photochemically formed unpaired electrons have been detected in electron-resonance spectra when prepared by u.v.-irradiation of a soln. frozen into a glass, and the identification of chemical species from resolved hyperfine structure is attempted. Details of solvents and technique are included. Spectra obtained by using the same crystal-video detector and X- and γ -irradiation are also discussed. The complete analysis of hyperfine structure for the purpose of identifying unknown groups is illustrated by work on stable organic radicals and the detection of impurity concn. in semi-conductors. A dynamic study in which the changing concn. of an unpaired electron-possessing intermediate could be followed by measuring the strength of the electron-resonance bands is mentioned, and the importance of simple spectra such as these is stressed in connection with structural analysis of large molecules.

E. G. CUMMINS

2.—INORGANIC ANALYSIS

1757. **Analysis of complexed insoluble salts by conductimetry.** C. Calmar. *Compt. Rend.*, 1956, **242** (11), 1465-1466.—Although AgI is virtually insoluble in water, it can be dissolved by the addition of KCN, forming a complex that exists only so long as there is an excess of KCN. If the solution is titrated by a strong acid (e.g., HCl), it is possible to follow the changes that take place by the variations in conductivity, and a curve can be plotted. With the example given, the conductivity drops as the acid combines with the excess of KCN. When this reaction is complete, the acid decomposes the complex, and pptn. of AgI occurs. The conductivity rises slowly during this reaction and, when all the AgI has been pptd., the addition of more titrant, producing an excess of acid, causes a sharp rise in conductivity. The method is applicable to all salts insoluble in water that will form soluble com-

plexes with cyanide or any other suitable substance, such as thiosulphate.

J. F. P. H. GREENE

1758. **Thermal decomposition of some metal formates.** V. Zapletal, J. Jedlička and V. Růžicka (Inst. Org. Technol., Vysoká škola chemická, Prague, Czechoslovakia). *Chem. Listy*, 1956, **50** (9), 1406-1409.—The temp. of dehydration and of decomposition of the formates of bivalent metals (Cu, Ni, Co, Zn, Cd, Mn, Hg, Ca, Sr and Ba), determined by the use of differential thermal analysis and gravimetric thermal analysis, are presented.

J. ZÝKA

1759. **Quantitative inorganic chromatography using rectified radio-frequency methods.** J. A. Broomhead and N. A. Gibson (Univ. Sydney, N.S.W., Australia). *Chem. & Ind.*, 1956, (49), 1474-1475.—Lithium, sodium and potassium have been separated by 2-ethylhexanol-methanol (3:7) on Whatman No. 3 paper (50 cm \times 2.5 cm), located by the rectified radio-frequency method of Blake (cf. *Anal. Chim. Acta*, 1956, **14**, 329) and then determined quantitatively by a conductimetric method. Quantities of about 1 mg each of Li, Na and K have been determined with an accuracy of 1.0%.

D. F. PHILLIPS

1760. **Determination of potassium as the meta-periodate.** R. E. Jentoft and R. J. Robinson (Univ. of Washington, Seattle, Wash., U.S.A.). *Anal. Chem.*, 1956, **28** (12), 2011-2015.—The Willard-Boyle method of determining K^+ as KIO_4 (cf. *Brit. Abstr. AI*, 1941, 279) has been modified to ensure greater accuracy. The sample, containing >75 mg of K, should contain only Na, Li and alkaline-earth cations (except Ba). Moderate amounts of Ca or Sr, or both, should be removed as oxalates before the K^+ are pptd. When large amounts of Na, Li, Ca or Sr are present, the K^+ are separated as potassium sodium cobaltinitrite, the ppt. is dissolved in hot 5 N HNO_3 , and the Na^+ are pptd. with oxalic acid and separated before pptn. of K^+ by dropwise addition of 50% (w/v) periodic acid. The pH of the soln. is afterwards adjusted to between 3.0 and 3.5 with 2.5 N lithium acetate soln. (2:6-dinitrophenol indicator), 2 ml of 95% ethanol is then added and the whole is kept at 0° for ≈ 40 min. The ppt. is collected in a Gooch crucible, and washed with the min. vol. of ethanol-isopropyl alcohol (2:1) at 0°. The KIO_4 is dissolved in 4 N H_2SO_4 and determined iodimetrically. The error caused by the solubility of KIO_4 is minimised by this procedure and can be corrected by reference to experimental curves. The final error is within $\approx \pm 0.1\%$ for K^+ concn. >3 mg; for concn. of 0.1 to 3 mg the error is within $\pm 0.005\%$. If ≈ 2.5 mg each of Na, Ca and Sr is present, the K^+ can be pptd. directly with HIO_4 .

W. J. BAKER

1761. **Amperometric titration of the tetraphenylboron ion. Method for potassium.** A. F. Findeis and T. De Vries (Purdue Univ., W. Lafayette, Ind., U.S.A.). *Anal. Chem.*, 1956, **28** (12), 1899-1901.—Potassium tetraphenylboron dissolved in methyl cyanide-water mixtures can be titrated with aq. standard AgNO_3 . A dropping-mercury electrode, at a potential of -0.1 V vs. the mercury-pool reference electrode, is used as the indicator. The method is suitable for between 1 and 20 mg of K, but could be extended to greater amounts; the greatest deviation obtained was 1.3%, but results were generally within 0.6%.

G. P. COOK

1762. The conductimetric precipitation titration of potassium with sodium tetraphenylboron. G. Jander and A. Anke (Anorg.-Chem. Inst., Tech. Univ., Berlin-Charlottenburg). *Z. anal. Chem.*, 1957, **154** (1), 8-17.—An aq. soln. of KCl is titrated with Na tetraphenylboron at room temp. and at a pH between 5 and 10. No interference is caused by Na^+ , Mg^{2+} and Ca^{2+} until their ratio to KCl is greater than 10:1. Twice this amount of Fe^{3+} is permissible. After quantitative removal of NH_4^+ by NaOH, the ammonia-free soln. may be titrated directly. The accuracy is that common to conductimetric techniques. M. F. C. LADD

1763. Rapid method of determining potassium oxide in glass by means of radioactivity. V. L. Indenbom, Ts. A. Karchmar, L. F. Yurkov and B. M. Glukhovskoi. *Zavod. Lab.*, 1956, **22** (11), 1293.—The method is based on the fact that natural K contains 0.011% of radioactive ^{40}K of very long half-life. With the apparatus used for finding the β -ray activity, 20 to 30 impulses per min. corresponded to 1% of K_2O in the glass. The content can be determined to within $\pm 0.15\%$ of the sample wt. G. S. SMITH

1764. Determination of small amounts of copper by the method of isotopic indication. N. A. Kiseleva, I. B. Megorskaya and M. I. Rozova (State Inst. of Applied Chem.). *Zavod. Lab.*, 1956, **22** (11), 1291-1292.—The method is based on the use of ^{151}I in a K_2HgI_4 soln. used for pptg. Cu as an *o*-phenylenediamine complex $[\text{Cu}(\text{C}_6\text{H}_5\text{N}_2)_2][\text{HgI}_4]$. The neutral soln. (1 ml) containing CuSO_4 is mixed with 0.1 to 0.2 ml of 2% *o*-phenylenediamine soln., one drop of 0.5 *N* H_2SO_4 and 0.05 to 0.10 ml of K_2HgI_4 soln. (prepared by adding 10% KI soln. containing ^{151}I to saturated HgCl_2 soln. until the ppt. first formed is redissolved). The ppt. is collected on a filter-paper, washed and dried. The paper is then coated with Cellophane lacquer on both sides and the activity is measured. The activity of the reagent soln. is also measured. The concn. of Cu in the ppt. can then be calculated. With 0.05 mg of Cu the results are accurate to within $\pm 3\%$. With smaller amounts of Cu a collector is necessary, e.g., $\text{Fe}_2(\text{SO}_4)_3$. G. S. SMITH

1765. New methods for the determination of copper in the presence of molybdenum. G. Spacu and C. Gheorghiu (Univ. "C.I. Parhon," Bucharest). *Rev. Chim. Bucurest.*, 1956, **1** (1), 15-20.—Two rapid, accurate methods are given for the determination of Cu and Mo in the same soln. (a)—The neutral or feebly acid soln. is treated at 60° with excess of H_2SO_4 , and a slight excess of NH_4SCN is added dropwise. The CuSCN is filtered off, washed with dil. H_2SO_4 , water, ethanol and ether and dried *in vacuo* for 10 min. before being weighed. Molybdenum is determined in the filtrate after evaporation to liberate SO_2 , oxidation of SCN^- with HNO_3 and removal of HNO_3 by evaporation with H_2SO_4 . It may either be reduced to tervalent Mo with Cd and H_2SO_4 , added to excess of ferric alum, and the Fe^{3+} titrated with KMnO_4 , or it can be pptd. with hydroxyquinoline and weighed. (b)—The neutral or feebly acid soln. (100 ml) is treated with 0.5 g of tartaric acid (to hold up Mo), 2 to 5 ml of pyridine and 0.5 g of NH_4SCN . The Cu dipyrindine thiocyanate is filtered off at once, washed with the same reagents in water, twice with pyridine- NH_4SCN in aq. ethanol, twice with pyridine in ethanol, once with pyridine in ether and dried *in vacuo* before being weighed. Molybdenum is

determined gravimetrically in the filtrate with hydroxyquinoline. The total time by either method is 4 hr. A. B. DENSHAM

1766. Specific colour test for silver ions, using pyrogallolsulphonephthalein (pyrogallol red) and its bromo derivative. Z. Vodák and O. Leminger (Org. Lab., Spolek pro chem. a hutní výrobu, Ústí nad Labem, Czechoslovakia). *Chem. Listy*, 1956, **50** (12), 2028-2029.—Silver ions yield with pyrogallolsulphonephthalein (I) and its dibromo deriv. (II) a golden-yellow coloration. This reaction may be used for the detection of Ag^+ in a test-tube or on paper. The interference of some elements can be eliminated by adding EDTA. *Procedure*—Add to the sample in a test-tube a few drops of I or II (0.1% soln. in 50% ethanol), set aside for 15 to 20 sec. with occasional shaking and make alkaline with aq. NH_3 . Only Au^{3+} yield a similar reaction, but they can be distinguished with SnCl_2 ; Na, K, NH_4^+ , Cu^{2+} , Be, Mg, Ca, Sr, Ba, Cd, Zn, Hg_2^{2+} , Ti^+ , Ce^{4+} , Pr^{3+} , Nd^{3+} , Pb^{2+} , Th^{4+} , As^{3+} , UO_2^{2+} , Cr^{3+} , Co^{2+} and Ni^{2+} when present in the same concn. do not interfere. When detecting Ag^+ in the presence of large concn. of Cu, Pb, Zn, Cd, Th, Nd and UO_2^{2+} , EDTA must be added. J. ZÝKA

1767. Determination of calcium in glass by flame photometry. D. Billings (Glass Containers Inc., Los Angeles, Calif., U.S.A.). *Glass Ind.*, 1955, **36** (5), 255-256, 280.—The presence of Al in the test soln. obtained by digesting the glass with HF and HClO_4 depresses the Ca emission; it must therefore be removed as $\text{Al}(\text{OH})_3$. Other interfering ions were either removed by pptg. the Ca as oxalate, redissolving and comparing with standards containing Ca in HCl soln., or were compensated for by the use of standards containing known amounts of Na and K. J. A. SUGDEN

1768. Determination of calcium in presence of a large excess of magnesium. V. Tichomírová and O. Šimáčková (Výzk. ústav stavebních hmot, Brno, Czechoslovakia). *Chem. Listy*, 1956, **50** (12), 1925-1927.—Magnesium can be masked with tartaric acid in strongly alkaline medium. This effect was used for the compleximetric determination of Ca in the presence of a large excess of Mg; a mixture of murexide and naphthol green was used as indicator. *Procedure*—Dilute a suitable amount of the sample to 200 ml, add tartaric acid (0.2 g) (sufficient for masking up to 50 mg of MgO), then hydroxylamine hydrochloride (0.05 g); adjust the pH to 12 by adding NaOH soln. and titrate as quickly as possible with 0.05 *M* EDTA (disodium salt), with the mixed indicator, to a blue end-point. The colour is stable for 10 sec. Determine Ca plus Mg in another sample by the usual compleximetric titration (Eriochrome black T as indicator). This method was used to analyse samples of dolomite, magnesite, magnesium silicates, etc. Silicic acid does not interfere if it is converted to the non-colloidal form by heating. The detailed procedure for various sorts of materials is given. J. ZÝKA

1769. Methods of analysis of calcium carbide and acetylene. I. I. Strizhevskii. *Zavod. Lab.*, 1956, **22** (11), 1297-1302.—A review with 28 references. G. S. SMITH

1770. Polarographic determination of traces of zinc in nickel sulphate. M. Kołodziejczak. *Chem. Anal., Warsaw*, 1956, **1** (2-3), 61-71.—Zinc is determined polarographically after being separated

from the bulk of the sample by dithizone extraction. Nickel is kept in the aqueous soln. during the extraction of Zn by the addition of KCN. *Procedure*—Dissolve 10 g of the nickel sulphate sample in a little water and 10 ml of conc. HCl and dilute with water to 100 ml. To 10 ml of the soln. add enough 10% KCN soln. to redissolve the originally formed ppt., then adjust the pH with dil. HCl to between 4 and 5. Add 1 g of Na acetate and extract the soln. with 0.01% dithizone in CCl_4 . Remove Zn from the solvent extract by shaking with dil. HCl, evaporate the acid soln., treat the residue with HNO_3 - H_2SO_4 and evaporate. Dissolve the residue in 10 ml of the base electrolyte (0.1 M acetic acid, 0.025 M KSCN), adjust the pH to 6, add two drops of 0.5% gelatin soln., transfer to the polarographic cell and remove dissolved oxygen. Polarograph in the usual way. The half-wave potentials are -1.0 V for Zn, -0.7 V for Ni and -0.4 V for Cu. The method was satisfactory for concn. of Zn between 0.001 and 0.1%; the error did not exceed 6% even at the lower concn. K. F. SPOREK

1771. Amperometric titration of cadmium with potassium iodide in the presence of excess of amidopyrine. A. K. Zhdanov, V. A. Khadeev and E. K. Makritskaya (V.I. Lenin Central Asiatic State Univ.). *Zavod. Lab.*, 1956, **22** (11), 1286-1291.—At low acidities (pH 2 to 5), amidopyrine (I) and KI give with Cd^{2+} a difficultly sol. complex $(\text{I})_2\text{CdI}_2$. The reaction can be used in the amperometric determination of Cd with KI at 1 V vs. the S.C.E. At higher acidities, $(\text{I})_2\text{H}_2\text{CdI}_4$ is formed. This is more sol. and cannot be used as a basis for amperometric titration. To determine Cd (<0.002 M), 25 ml of the soln. is mixed with I (5 to 10 times the molar concn. of the Cd), then neutralised to methyl orange indicator and titrated with KI soln. after removal of O by the passage of N. The cathode is a dropping-mercury electrode and the anode is a S.C.E. joined to the soln. by means of an agar- KNO_3 bridge. No interference is caused by the presence of Zn^{2+} , Mn^{2+} , Ni^{2+} , Co^{2+} , NH_4^+ , SO_4^{2-} , NO_3^- , acetate and tartrate. The interference of Pb is prevented by addition of Na_2SO_4 , and the interference of Bi is prevented by addition of aq. NH_3 followed by titration in the presence of the ppt. With Cd and Zn together the Cd can be titrated first in the presence of I, and then the Zn can be titrated at -1.3 V with EDTA after addition of Na acetate to make the concn. of the latter ≈ 0.1 M. To determine Zn and Cd in an alloy containing Al, Zn, Cd and Mn, the sample is dissolved in dil. H_2SO_4 (1 + 5), Zn and Cd are separated by means of H_2S , the ppt. is dissolved in dil. H_2SO_4 , and Cd and Zn are successively determined amperometrically in one aliquot portion. G. S. SMITH

1772. Polarographic determination of cadmium in lithium nitrate ammine $[\text{LiNO}_3 \cdot n\text{NH}_3]$. W. Hubicki and Z. Zychiewicz (Lublin Univ., Poland). *Ann. Univ. M. Curie-Skłodowska, [A]*, 1954, (1956), **9**, 71-82.—Lithium nitrate gives a liquid product with dry NH_3 of limiting composition $\text{LiNO}_3 \cdot 4\text{NH}_3$, which is stable below 70° , and behaves like a soln. of LiNO_3 in liquid NH_3 . Solutions of $\text{Cd}(\text{NO}_3)_2$, CdCl_2 and Cd acetate in this fluid at 8° are suitable for the polarographic determination of Cd^{2+} ; the i_d vs. $[\text{Cd}^{2+}]$ curves are linear, and the $E_{1/2}$ is -0.78 V. R. TRUSCOE

1773. Spectrochemical determination of aluminium in iron-aluminium alloys. E. F. Runge and F. R. Bryan (Ford Motor Co., Dearborn, Mich.,

U.S.A.). *J. Metals*, N.Y., 1956, **8**; *Trans.*, **206**, 1674-1676.—Rod samples 5.0 mm in diam. are excited by a high-voltage controlled spark, with a counter electrode of pure iron and flushing the analytical gap with N during excitation. The spectra are photographed and the intensity ratios of a pair of lines, one from Al and one from the internal standard Fe, are determined. The photographic emulsion is calibrated by means of a set of standard Fe arc lines for which relative intensities are known. The concn. of Al is obtained from a graph, prepared from standard samples, relating the log intensity ratio of the line pair to the log of the concn. S.C.I. ABSTR.

1774. Spectrographic analysis of aluminium anti-friction alloy ASM. V. V. Kuznetsova and K. E. Sergeeva (Moscow Works for the Treatment of Non-ferrous Metals). *Zavod. Lab.*, 1956, **22** (11), 1319-1320.—Conditions for spectrographic determination by spark excitation of Sb, Mg, Fe, Si, Cu and Mn in aluminium alloys containing 1 to 6% of Sb and 0.1 to 1% of Mg are described. G. S. SMITH

1775. Gas content of solid aluminium by solid extraction and vacuum fusion. J. L. Brandt and C. N. Cochran (Physical Chemistry Div., Aluminum Co. of America, New Kensington, Pa.). *J. Metals*, N.Y., 1956, **8**; *Trans.*, **206**, 1672-1674.—Two methods for the determination of H in aluminium are described. In the solid extraction method, the sample is heated to $\approx 50^\circ$ below its m.p. in a Vycor extraction tube connected to the analytical part of the system. In the vacuum-fusion method, the melting assembly consists of a graphite crucible insulated from an outer quartz envelope by boron nitride powder. A second graphite crucible inside the first holds the melted sample. Heating is by high-frequency induction. Results are given which show good agreement between the two methods. S.C.I. ABSTR.

1776. Polarographic determination of traces of metals in pure aluminium. M. Węclewska and M. Picheń (Mining Institute, Stalingrad). *Chem. Anal., Warsaw*, 1956, **1** (2-3), 72-75.—The determination of traces of Zn, Pb, Cu, Fe and Mn in pure aluminium is described. A soln. of the sample in HCl is saturated with NH_4Cl , and used directly for the determination of Zn at -1.4 V, and Pb at about -0.5 V. Copper, Fe and Mn were determined after the addition to the original soln. of aq. NH_3 , glycerol and gum acacia in the ratio 1:2:1; at -0.2 to -0.5 V, -1.6 V and -1.7 V, respectively. Concentrations of these metals $<0.01\%$ were determined by co-pptn. with $\text{Al}(\text{OH})_3$, dissolving in HCl and testing polarographically. K. F. SPOREK

1777. Analysis of pickling-bath solution [for aluminium] using ion exchange. F. Nesh and E. C. Haas (New York Naval Shipyard, N.Y., U.S.A.). *Anal. Chem.*, 1956, **28** (12), 2034.—A more rapid routine method of analysing pickle-liquor used for cleaning aluminium or its alloys (5 ml of sample diluted to 250 ml) involves titration to pH 3.5 for HNO_3 content, followed by titration to pH 7 for $\text{Al}(\text{NO}_3)_3$ content. The content of Na_2SO_4 is determined by passing 25 ml of the diluted soln. through a column of Amberlite IR-100 (40 g, H form) in a 100-ml burette (cf. Fisher et al., *Anal. Abstr.*, 1956, **3**, 721). The percentage of Na_2SO_4 is calculated, by difference, from the total cation value of the eluate. W. J. BAKER

1778. Polarographic behaviour of gallium. E. N. Vinogradova and N. N. Chudinova (Moscow State Univ.). *Zavod. Lab.*, 1956, **22** (11), 1280-1284.—In soln. of ClO_4^- , NO_3^- , Cl^- , SO_4^{2-} , acetate, citrate, sulphosalicylate and EDTA, $E_{1/2}$ for Ga corresponds to the reduction potential of H, and the polarographic determination of Ga is unsatisfactory. In $<0.003 M$ salicylate at pH 2.8 to 3.4, Ga gives a wave with $E_{1/2}$ of $-0.88 V$ vs. the S.C.E., which can be used for its determination. Large amounts of SO_4^{2-} , NO_3^- and Cl^- do not interfere. The wave height is proportional to the concn. over the range 0.028 to 1.4 mM. The reduction is irreversible.

G. S. SMITH

1779. Flame-spectrophotometric determination of gallium in copper-gallium alloys. V. W. Meloche and B. L. Beck (Univ. of Wisconsin, Madison, U.S.A.). *Anal. Chem.*, 1956, **28** (12), 1890-1891.—Two procedures are given, one for the determination of 0 to 1% of Ga in Ga-Cu alloys with an error $\pm 0.01\%$ and a mean absolute deviation of 0.003%, the other for 0 to 10% of Ga with an error $\pm 0.1\%$ and a mean absolute deviation of 0.1%. Copper is added to the standard solutions of Ga so as to increase the emission of the 417.2-m μ line of Ga. In all instances, a 1-g sample is dissolved in the min. vol. of HNO_3 and the soln. is diluted to either 100 or 1000 ml with the addition of 0.04% Sterox SE to eliminate drift of spectrophotometer readings. More than 50 p.p.m. of Fe interferes seriously and >500 p.p.m. of Zn, Al or In only slightly.

W. J. BAKER

1780. Use of the chromatographic method for separating gallium from other elements. Separation of gallium and zinc. I. P. Alimarin and E. P. Tsintsevich (Moscow State Univ.). *Zavod. Lab.*, 1956, **22** (11), 1276-1279.—The soln. containing Ga and Zn together with a complexing agent was passed through a 75-mm column 1 cm wide containing 10 g of SBS resin of grain size 0.5 to 1 mm in the H or the NH_4 form. In tartrate soln. at pH 9 to 10, Zn is wholly and Ga partially retained by the H form of the resin, whilst Zn is wholly retained and Ga is wholly unadsorbed by the NH_4 form of the resin. A six to ten-fold excess of tartaric acid is required. Zinc can be extracted from the column by means of 10% HCl soln. The separation is just as satisfactory in the presence of oxalate, sulphosalicylate or EDTA instead of tartaric acid. In the presence of a twofold excess of EDTA at pH 4 to 5, satisfactory separation on the resin in the H form is obtained. The separation of a soln. (50 ml) containing 4.9 mg of Ga, 50.2 mg of Zn, 10 mg of Fe and 10 mg of Cu was obtained by passing the soln. through SBS in the H form to retain all the cations, then extracting the Ga and Zn with 10% NaOH soln., and separating the Ga and Zn by the EDTA method.

G. S. SMITH

1781. Spectrographic determination of indium in iron-base samples. N. A. Yarosh, G. P. Skornyakov and K. A. Efremova (Inst. of Metal Physics, Ural Filial, Acad. Sci., U.S.S.R.). *Zavod. Lab.*, 1956, **22** (11), 1314-1315.—The sample (20 to 25 mg) is mixed with 10 to 15 mg of NaCl (to suppress the cyanogen bands) and placed in the hollow of a carbon electrode. The spectrum is excited by means of a 5-amp. d.c. arc between the sample and an upper carbon electrode, and the line In 4511.32 Å is compared with the background. All indium lines in the u.v. are interfered with by Fe. Concn. of In

of 0.0025 to 0.025% in the presence of high concn. of Fe can be determined with an error of $\pm 10\%$.

G. S. SMITH

1782. Photometric titration of cerium(III). T. L. Marple, E. P. Przybylowicz and D. N. Hume (Mass. Inst. of Technol., Cambridge, U.S.A.). *Anal. Chem.*, 1956, **28** (12), 1892-1894.—A rapid and accurate method for the direct photometric titration of Ce^{III} in the presence of large amounts of Ce^{IV} is described. It is based on the oxidation of Ce to Ce^{IV} with permanganate in a neutral pyrophosphate medium. The levels of concn. studied ranged from about 6 to 89 mg per 85 ml of soln., and the coeff. of variation was 0.4%. Reducing agents such as Hg^{II} , V^{IV} , As^{III} , Sb^{III} , Ti^{II} and I^- interfere, as do substances that form ppt., e.g., Cr^{III} and F^- .

K. A. PROCTOR

1783. Differential spectrophotometric determination of neodymium in neodymium-yttrium mixtures. C. V. Banks, J. L. Spooner and J. W. O'Laughlin (Inst. for Atomic Research and Dept. of Chemistry, Iowa State College, Ames, U.S.A.). *Anal. Chem.*, 1956, **28** (12), 1894-1897.—The method has been used for the analysis of mixtures of Nd_2O_3 and Y_2O_3 in which the content of Nd varied from 10 to 80%. The method can be used for very small samples, the limiting factor being the necessity of having a final vol. great enough to fill a 1-cm cell. The error in concn. is about 0.25%.

K. A. PROCTOR

1784. Compleximetric determination of the rare earths. G. Brunisholz and R. Cahen (Lab. Chim. Minérale et Anal., Univ., Lausanne). *Helv. Chim. Acta*, 1956, **39** (7), 2136-2137.—A slightly acid solution of the chlorides or nitrates of the rare earths ($\approx 0.01 M$) is treated with 2 to 3 g of hexamine to act as buffer and then titrated with the ammonium salt of EDTA in 0.01 M solution, with Eriochrome black T as indicator. If Ce is present, 10 mg of ascorbic acid (or hydroxylamine hydrochloride) is added to inhibit oxidation of Ce^{III} to Ce^{IV} . Traces of Fe^{3+} , or other polyvalent metal ions, interfere with the titration. (Cf. *Anal. Abstr.*, 1956, **3**, 2674.)

S.C.I. ABSTR.

1785. Co-precipitation of rare-earth iodates with thorium iodate precipitated from homogeneous solution. K. J. Shaver (Monsanto Chem. Co., Miamisburg, Ohio, U.S.A.). *Anal. Chem.*, 1956, **28** (12), 2015-2019.—The efficiency of separation of Th from rare earths by pptn. of $\text{Th}(\text{IO}_3)_4$ from homogeneous soln. was investigated, the degree of co-pptn. with La, Ce, Pr, Pm, Sm, Eu, Y and Sc being determined with radioactive tracers of these elements. The trivalent rare-earths are co-pptd. with $\text{Th}(\text{IO}_3)_4$ by isomorphous replacement in the iodate lattice, the extent of co-pptn. depending on the ionic radii (from Sc 0.68 Å to La 1.04 Å). For a pptn. of Th of 99.96%, and in the presence of a carrier, co-pptn. varies from 0.08% for Y to 0.49% for La. The distribution law for La and Pr with Th is logarithmic, so that max. possible separation can be achieved.

W. J. BAKER

1786. Use of iodine chloride in analytical chemistry. V. Determination of cyanides and thiocyanates. J. Čihálik and K. Terebová (Inst. Anal. Chem., Charles' Univ., Prague, Czechoslovakia). *Chem. Listy*, 1956, **50** (11), 1761-1767.—By using 0.1 M ICl, cyanides in NaHCO_3 soln. can be titrated visually (starch indicator) or potentiometrically. An excess of Cl^- or Br^- does not cause interference; iodides in greater than tenfold excess must be

absent. Thiocyanate can be titrated in slightly acid soln. (0.5% HCl) or in NaHCO_3 soln., with an average error of $\pm 0.5\%$ or 0.34% , respectively. To determine a mixture of cyanides and thiocyanates, first titrate the CN^- plus SCN^- in NaHCO_3 soln., then add acid to a second aliquot, remove CN^- by heating, add an excess of NaHCO_3 and titrate the SCN^- . J. ŽYKA

1787. Determination of impurities in silicon by neutron activation analysis. A. Kant, J. P. Cali and H. D. Thompson (Air Force Cambridge Res. Center, Bedford, Mass., U.S.A.). *Anal. Chem.*, 1956, **28** (12), 1867-1871.—The determination of P, Fe, Cu, Zn, Ga, As, Ag, Cd, In, Sb, Tl and Bi in silicon in the concn. range 10^{-2} to 10^{-5} p.p.m. is described. After radiochemical separation the elements are characterised and determined by their induced beta-activities. The overall error of the method is estimated to be about 50% for the absolute method and 10% for the comparative method. K. A. PROCTOR

1788. Determination of specific surface area of colloidal silica by titration with sodium hydroxide. G. W. Sears, jun. (Grasselli Chem. Dept., E.I. du Pont de Nemours & Co., Inc., Wilmington, Del., U.S.A.). *Anal. Chem.*, 1956, **28** (12), 1981-1983.—The specific surface-area (S) of colloidal particles ($<10 \mu\text{m}$) of SiO_2 can be determined rapidly by titrating a suspension of a 1.5-g sample in 150 ml of 20% aq. NaCl at pH 3 to 3.5 and 25°. The titrant is 0.1 N NaOH and the base is added until the pH rises to a const. value of 9 (glass electrode and S.C.E.). At pH 9 there are adsorbed 1.26 OH^- per sq. μm of surface; S (sq. m. per g) is calculated as $32 V - 25$, where $V = \text{ml of } 0.1 \text{ N NaOH}$ used to raise the pH from 4 to 9. The reproducibility is within 5% and the accuracy, for particles $<5 \mu$ diam., is greater than for the N-adsorption method. Unless their concn. are known, weak electrolytes (e.g., containing NH_4^+ , Fe, Al) should be absent. The method is applicable to ignited silica gel and other prep. of SiO_2 provided that the sample is ground to -100 mesh before it is added to the NaCl soln. W. J. BAKER

1789. Colorimetric determination of germanium in ammonia liquor. Shigenori Takano and Kiyoshi Saito (Nippon Iron & Pipe Co., Kawasaki). *Coal Tar, Japan*, 1955, **7**, 456-460.—Measure 50 ml of ammonia liquor into a distilling flask, add 50 ml of conc. HCl, heat nearly to boiling-point, add slowly 15 ml of 10% KClO_4 soln. and distil the mixture. When the distillate collected is $\approx 30 \text{ ml}$, add 25 ml of conc. HCl and continue the distillation until the contents of the flask are about 40 ml. Transfer the distillate into a 50-ml volumetric flask, make up to vol. and filter through dry filter-paper. Measure 20 ml of the filtrate into a 100-ml volumetric flask, add powdered NaHSO_4 little by little until the yellow colour is discharged, add bromine water until the soln. turns yellow, and again reduce with NaHSO_4 . Add 5 ml of 0.5% gelatin soln., cool with water to about 20°, add 15 ml of 0.03% phenylfluorone soln. in ethanol, dilute to 100 ml and, after shaking for 15 min., compare the extinction with that of the blank soln. containing the same amounts of the reagents. The quantity of Ge in the sample is determined from extinction - concn. curves. CHEM. ABSTR.

1790. Microcrystalloscopic reaction for tin. R. K. Korabel'nik (Moscow Inst. of Steel). *Zavod. Lab.*, 1956, **22** (11), 1297.—The microscopical detection of

Sn^{4+} can be carried out by treating a drop of the chloride soln. with a drop of 2 N aq. NH_3 , followed by a drop of 2 N HCl if the soln. has become cloudy, heating until a ring of salts forms and then examining the octahedral crystals of $(\text{NH}_4)_2[\text{SnCl}_6]$ that appear within 2 min. The minimum amount of Sn detectable is $0.05 \mu\text{g}$, at a limiting dilution of 1 in 2×10^4 . With Sn^{4+} , oxidation with H_2O_2 is necessary. No interference is caused by K, Na, Mg, Ba, Ca, Sr, Fe^{3+} , Fe^{2+} , Zn, Al, Cr^{3+} , Co, Ni, Mn, Pb, Ag, Hg, Cu, Cd, Bi, Sb, As, Ti, V, Mo or W. G. S. SMITH

1791. Compleximetric titrations (chelometry). **XXIV. Determination of lead using catechol violet as indicator.** J. Vřešťál and J. Havří (Military Tech. Acad., Brno, Czechoslovakia). *Chem. Listy*, 1956, **50** (11), 1851-1853.—The titration of Pb^{2+} in soln. buffered with hexamine can be carried out with an ammoniacal soln. of EDTA as volumetric reagent, and catechol violet as indicator. *Procedure*—Neutralise the soln. of the sample (100 ml) containing 1 to 500 mg of Pb with dil. aq. NH_3 , and when a turbidity appears add dil. HNO_3 (one drop) and catechol violet soln. (0.1%) (two drops), and hexamine soln. (10%) till the soln. turns blue. Titrate with EDTA till the colour changes to grey, and add hexamine soln. (1 ml) (the colour reverts to blue); continue with the titration till a yellow colour appears. There is no interference from Mg, Sr and Ba; in the presence of Ca the colour change is not sharp. To prepare the volumetric soln., dissolve EDTA (32 g) in H_2O and titrate with 1 N aq. NH_3 (methyl red indicator). Then add 92% of this required vol. of 1 N aq. NH_3 and dilute to 1 litre. This soln. should not cause a change in pH of CaCl_2 soln. neutralised to a mixture of methyl red and methylene blue (pH 5.5). When necessary, add dil. HNO_3 or aq. NH_3 . J. ŽYKA

1792. Compleximetric titrations (chelometry). **XXV. Determination of lead with Brilliant Congo blue in unbuffered solution.** J. Vřešťál and S. Kotrlý (Military Tech. Acad., Brno, Czechoslovakia). *Chem. Listy*, 1956, **50** (11), 1775-1779.—Brilliant Congo blue (I) was used as a chelometric indicator for the determination of Pb^{2+} in neutral soln., an ammoniacal soln. of EDTA (II) being used as volumetric reagent; the addition of buffer soln. is not necessary. *Procedure*—Adjust the soln. of lead salt (10 to 250 mg of Pb) with aq. NH_3 to pH 5, dilute to 75 ml, add a very small amount of I and titrate with an ammoniacal soln. of II. Near the equiv. point add, with stirring, 2 to 4 drops of 0.1 N aq. NH_3 and titrate till the colour changes to blue. The presence of Ag^+ , Mg^{2+} , NH_4NO_3 , KNO_3 , NaNO_3 , acetates and small amounts of Cl^- does not cause interference. The preparation of the volumetric reagent, whose stability is satisfactory, is described. The absorption curves of I and of its complex with Pb were recorded, and the possibility of determining the equiv. point by photometric titration was studied. J. ŽYKA

1793. Polarographic determination of oxidised lead in metallic lead. Z. Zagórski. *Chem. Anal., Warsaw*, 1956, **1** (2-3), 80-90.—Metallic lead is usually contaminated by small quantities of O, which may be present as lead oxide or dissolved O. By the method described, concn. of about 10 g of O per ton of lead can be determined. The lead was dissolved in mercury, 0.4 N HCl was added, the soln. electrolysed, and the Pb determined at

intervals polarographically. By extrapolation to zero time, the oxidised Pb was calculated.

K. F. SPOREK

1794. Polarographic determination of lead in liquid ammonium nitrate ammine [Divers' fluid]. W. Hubicki and J. Matysik (Lublin Univ., Poland). *Ann. Univ. M. Curie-Skłodowska*, [A4], 1954, [1956], 9, 1-7.—The E_1 of Pb^{2+} in Divers' fluid at 0° is -0.35 V, and the height of the polarographic wave is proportional to $[Pb^{2+}]$ for concn. up to 3.4 g per litre for $PbSO_4$, PbI_2 , $PbCl_2$, $Pb(NO_3)_2$ and $PbCrO_4$.

R. TRUSCOE

1795. Spectrographic analysis of lead. I. G. Yudelevich, V. G. Kovaleva and A. L. Levitina (M.I. Kalinin Chimpent Lead Works). *Zavod. Lab.*, 1956, 22 (11), 1310-1312.—Conditions for determining Bi, Sb, Sn, Cu, Zn, Ag, As, Mg, Ca, Na and Fe in metallic lead by means of spark and arc excitation are described.

G. S. SMITH

1796. Analytical reactions of salicylic acid and its derivatives and a spectrophotometric investigation of the Ti^{4+} -sulphosalicylic acid complexes. L. Sommer (Inst. Anal. Chem., Masaryk Univ., Brno, Czechoslovakia). *Chem. Listy*, 1956, 50 (11), 1702-1710.—The mechanism of the reactions of Ti^{4+} with salicylic, sulphosalicylic, 2,4-dihydroxybenzoic, *p*-aminosalicylic and 2-hydroxy-*p*-toluic acids has been studied.

J. ŽYKA

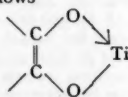
1797. Spectrophotometric study of the complexes of titanium with chromotropic acid and 1:8-dihydroxynaphthalene. A. Okáč and L. Sommer (Inst. Anal. Chem., Masaryk Univ., Brno, Czechoslovakia). *Chem. Listy*, 1956, 50 (11), 1711-1728.—Chromotropic acid has been found to be the best reagent for the detection of Ti^{4+} ; Fe^{3+} interfere, but can be reduced with ascorbic acid. The formation and the characteristics of the complex of Ti^{4+} with chromotropic acid were studied.

J. ŽYKA

1798. Analytical reactions of some *o*-diphenols and a spectrophotometric investigation of the complexes of titanium with catechol and catechol-3:5-disulphonic acid. L. Sommer (Inst. Anal. Chem., Masaryk Univ., Brno, Czechoslovakia). *Chem. Listy*, 1956, 50 (11), 1729-1745.—In coloured, slightly acid soln. of Ti^{4+} with catechol (I) and catechol-3:5-disulphonic acid (II) (tiron), various complexes were identified. The results of the spectrophotometric investigations (continual variations, photometric titration, logarithmical analysis, analysis of pH curves) prove that the reaction mechanism seems to be analogous with that found by studying the reactions of Ti^{4+} with chromotropic acid (Okáč *et al.*, *Anal. Abstr.*, 1957, 6, 1797).

J. ŽYKA

1799. The analytical functional group for Ti^{4+} . A. Okáč and L. Sommer (Inst. Anal. Chem., Masaryk Univ., Brno, Czechoslovakia). *Chem. Listy*, 1956, 50 (11), 1746-1748.—The reactions of 37 aliphatic and aromatic hydroxy compounds with Ti^{4+} were examined, and the conclusion was reached that the analytical functional group for titanium can be formulated as follows



Increasing stability of the chelate increases also the sensitivity of the reaction. Chromotropic acid has

been found to be the most suitable of all examined compounds, because of the presence of sulpho groups, which increase the stability of the chelate with Ti^{4+} .

J. ŽYKA

1800. Determination of bivalent-titanium. S. F. Belov and D. N. Ivanova. *Zavod. Lab.*, 1956, 22 (12), 1415-1417.—The determination of Ti^{II} from the amount of Fe^{III} that it can reduce is unsatisfactory since some H is likely to be formed. A method based on the vol. of H liberated in the reaction $2TiCl_2 + 2HCl = 2TiCl_3 + H_2$ is recommended. A suitable reaction vessel with measuring tube is described. The difference between parallel determinations does not exceed 3.8% of the content. The soln. obtained can subsequently be used for the determination of Ti^{III} .

G. S. SMITH

1801. Microcrystalloscopic determination of titanium with diantipyrinyl-*o*-hydroxyphenylmethane [salicylidenediphenazone]. R. G. Belles (Gorno-Altai Pedagog. Inst.). *Zavod. Lab.*, 1956, 22 (11), 1296.—Salicylidenediphenazone (I) hydrochloride, obtained from salicylaldehyde and phenazone, reacts in neutral or weakly acidic medium with Ti^{4+} in the presence of NO_3^- , ClO_4^- , SCN^- or I^- to give pale-yellow difficultly sol. needles having the formula $2I \cdot TiOx_2$, where X is NO_3^- , etc. The minimum amount of Ti that can be detected in 0.2 to 0.3 ml is 2 to 3 μg , at a limiting dilution of 1 in 1×10^5 . No interference is caused by Al^{3+} , Fe^{3+} , Fe^{2+} , Mn^{2+} , Ni^{2+} , Co^{2+} , Cr^{3+} , Sn^{2+} , VO_3^- , Pb^{2+} , Cu^{2+} and Zr^{4+} .

G. S. SMITH

1802. Determination of titanium in titanium ores and metal by automatic derivative spectrophotometric titration. H. V. Malmstadt and C. B. Roberts (Univ. of Illinois, Urbana, U.S.A.). *Anal. Chem.*, 1956, 28 (12), 1884-1886.—A rapid method of determining Ti in ilmenite, rutile, titanium sponge or commercial TiO_2 , with an error $\pm 0.1\%$, is described. After dissolution of the sample, an aliquot of the soln. is passed through a cadmium reductor and collected in a soln. containing a known amount of Fe^{3+} in ≈ 0.5 M HCl. The Ti^{3+} reduce an equiv. amount of Fe^{3+} , the excess of the Fe^{3+} being automatically titrated by the derivative spectrophotometric end-point detection procedure (*Idem.*, *Ibid.*, 28, 1408). The titration with electrolytically generated Ti^{3+} is made at $\approx 78^\circ$ after boiling the soln. for 5 min. With ores for which the content of Ti is known approx., the end-point can well be detected visually. The standard soln. of Fe^{3+} (0.62 or 1.25 g per 500 ml) should contain 20 mg of Ti^{4+} per ml to ensure max. current efficiency. There is no interference from Fe, Mn, Mg or $<1\%$ of Cr, but Mo, Sn, V and Cu should be removed from alloy samples.

W. J. BAKER

1803. Chelatometry. XIII. The masking of titanium (IV) ions. P. Wehber (Lab. Metallhütte Mark A.-G., Hamburg-Wilhelmsburg, Germany). *Z. anal. Chem.*, 1957, 154 (3), 182-185.—Compleximetric reactions are not specific, consequently the masking of interfering ions is important. The successful masking of considerable concn. of Ti^{4+} at pH 10 has hitherto not been possible. The complex anion of tetraperoxyorthotitanic acid was found to be stable in the presence of EDTA and Eriochrome black T indicator at pH 10. From the acid soln. containing titanyl ions the complex anion is formed by the addition of H_2O_2 , followed by NaOH. The intense orange peroxytitanyl ion is formed first— $[TiO.aq.]^{2+} + H_2O_2 \rightleftharpoons [TiO_2.aq.]^{2+} + H_2O$. On addition of the alkali a colour change

from orange to yellow takes place at pH ≈ 3.5 . At pH 10 the solution is faintly yellow— $[\text{TiO}_2\text{aq.}]^{3+} + 3\text{H}_2\text{O}_2 \rightleftharpoons [\text{Ti}(\text{O}_2)_4\text{aq.}]^{4-} + 6\text{H}^+$. The method was applied to the titration with EDTA of zinc in the presence of titanyl ions. Analysis of the results showed good agreement between zinc added and zinc determined for mixtures of Zn and Ti (1:10). The max. advisable concn. of titanium is 100 mg of Ti per 100 ml of soln. Disadvantages of the method are: (1) H_2O_2 quickly decomposes the indicator at pH 10 and rapid titration is therefore essential; (2) ferric iron interferes since it decomposes the alkaline H_2O_2 . L. S. ADLER

1804. Indirect determination of free titanium and of oxygen in titanium - oxygen alloys by hydrogen evolution method. M. E. Straumanis, C. H. Cheng and A. W. Schlechten (Univ. Missouri School of Mines and Metall., Rolla, U.S.A.). *Anal. Chem.*, 1956, **28** (12), 1883-1884.—The amount of free Ti in pure Ti-O alloys can be calculated from the vol. of H evolved by dissolution of the sample in 3 N to 6 N HF. The content of O can be calculated indirectly from the lesser vol. of H evolved because of the presence of O in the sample. The results are within 1% of those obtained by Rahm's method (*Brit. Abstr. C*, 1953, 109). The procedure takes ≈ 1 hr. and is limited to alloys containing $\geq 33\%$ (by wt.) of O. W. J. BAKER

1805. Determination of bi- and ter-valent titanium in fused alkali-metal chlorides after electrolysis. E. G. Tabakova and Z. V. Solov'eva (Central Sci. Res. Inst. of Ferrous Metall.). *Zavod. Lab.*, 1956, **22** (12), 1417-1419.—The contents of Ti^{2+} and Ti^{3+} are found by calculation from the results of two titrations. One portion of the sample is dissolved in excess of a soln. of Fe^{3+} , and the Fe^{2+} formed are titrated with KMnO_4 . Another portion is dissolved in 0.1 N HCl, whereby Ti^{2+} are oxidised to Ti^{3+} and H is liberated, excess of a soln. of Fe^{3+} is added and the Fe^{2+} formed are titrated with KMnO_4 . *Procedure*—In an atmosphere of CO_2 dissolve 1 g of sample in 25 ml of cold 20% ferric ammonium alum containing 1 ml of conc. H_2SO_4 in 100 ml, then add 75 ml of dil. H_2SO_4 soln. (1 + 20) and 5 ml of Reinhardt's mixture, and titrate to a stable pink colour with 0.02 N KMnO_4 (V_1 ml). Also in an atmosphere of CO_2 dissolve 1 g of sample in 100 ml of 0.1 N HCl in the presence of 5 ml of saturated $(\text{NH}_4)_2\text{SO}_4$ soln. to act as a stabiliser of Ti^{3+} , then add 75 ml of dil. H_2SO_4 soln. (1 + 20) and 5 ml of Reinhardt's mixture, followed by 25 ml of 20% ferric ammonium alum soln., and titrate with 0.02 N KMnO_4 (V_2 ml). The content of Ti^{2+} corresponds to $2(V_1 - V_2)$ and that of Ti^{3+} to $2V_2 - V_1$. The determinations can be carried out in 20 to 30 min. G. S. SMITH

1806. Determination of magnesium and iron in titanium and its alloys. L. M. Budanova, L. A. Nenasheva and T. V. Matrosova. *Zavod. Lab.*, 1956, **22** (12), 1419-1421.—Magnesium is determined colorimetrically with *p*-nitrophenylazoresorcinol (I) at a pH > 12 in the presence of excess of H_2O_2 to prevent the interference of Ti. Titan yellow cannot be used under these conditions. Iron is determined colorimetrically with *o*-phenanthroline, which is added to a soln. of the alloy in HCl subsequently treated with hydroxylamine so that Ti^{3+} are oxidised whilst Fe remains as Fe^{3+} . *Procedure for magnesium*—The sample (1 g) containing 0.025 to 1.0% of Mg is dissolved in 75 ml of conc. HCl and the soln. is filtered and made up to 250 ml in a

calibrated flask. An aliquot portion (2 ml) in a graduated tube is treated with 1 to 2 ml of water, ten drops of 30% H_2O_2 and sufficient 2% NaOH soln., added dropwise, to decolorise the soln. After addition of 2 ml of a 0.001% soln. of I in 2 N NaOH, eight to ten drops of 20% NaOH soln. are added and then water to give a vol. of 10 ml. The colour is compared with a scale of standards. No interference is caused by the presence of 0.3% of Fe and Cr. *Procedure for iron*—The sample (1 g) containing 0.02 to 3% of Fe is dissolved in 75 ml of conc. HCl and the filtered soln. is made up to 250 ml. An aliquot portion (10 ml) in a 100-ml calibrated flask is treated with 2 ml of 10% hydroxylamine hydrochloride soln. and neutralised to Congo red paper with 2 N Na acetate. A 0.25% aq. soln. (10 ml) of *o*-phenanthroline (2:2'-dipyridyl can be used) is added, the soln. is diluted to 100 ml, and the colour intensity is measured through a green filter after 15 to 20 min. The content is found from a calibration curve. G. S. SMITH

1807. Determination of chloride in titanium sponge by the rapid potentiometric method. H. V. Malmstadt, E. R. Fett and J. D. Winefordner (Univ. of Illinois, Urbana, U.S.A.). *Anal. Chem.*, 1956, **28** (12), 1878-1882.—The two alternative procedures given for the rapid and accurate determination of 0.001 to 0.5% of Cl^- in titanium sponge depend on a final potentiometric measurement of the voltage difference between two silver-silver chloride electrodes in a concentration cell, one arm of which contains the sample soln. and the other a 10^{-3} M soln. of Cl^- in $\text{M H}_2\text{SO}_4$. In one procedure the Cl^- are removed from an aliquot of a H_2SO_4 soln. of the sample by rapid distillation. In the second method the metal is dissolved in a mixture of conc. H_2SO_4 , 48 to 50% HBF_4 and H_2O , and treated with hydroxylamine sulphate to oxidise selectively Ti^{3+} , and not Fe^{2+} . Each procedure takes only 5 to 7 min. after dissolution of the metal. W. J. BAKER

1808. Quantitative micro-determination of gaseous ammonia by its absorption at 204.3 μm . F. A. Gunther, J. H. Barkley, M. J. Kolbezen, R. C. Blinn and E. A. Staggs (Citrus Exp. Sta., Univ. California, Riverside, U.S.A.). *Anal. Chem.*, 1956, **28** (12), 1985-1989.—By using the absorption max. at 204.3 μm , concn. of 7 to 1000 p.p.m. of NH_3 in air can be determined by a direct spectrophotometric method. At the lowest concn., 10-cm cells are necessary. Modifications to the Beckman DU spectrophotometer to adapt it for these determinations are described, and comparisons are made of fused silica and crystal quartz spectrophotometers for this purpose. K. A. PROCTOR

1809. Use of iodine chloride in analytical chemistry. VI. Determination of hydrazine, phenylhydrazine, hydroxylamine and iodine chloride. J. Čihálik and K. Terebová (Inst. Anal. Chem., Charles' Univ., Prague, Czechoslovakia). *Chem. Listy*, 1956, **50** (11), 1768-1774.—Aq. soln. of hydrazine sulphate can be titrated potentiometrically with ICl soln. with an error of $\pm 0.35\%$. In a soln. of Na acetate, starch may be used as indicator. The method in reverse can be used for the standardisation of a soln. of ICl . Phenylhydrazine hydrochloride can be titrated with ICl in aq. soln. Hydroxylamine can be determined indirectly; an excess of ICl can be determined with a standard soln. of hydrazine sulphate. Numerous results are given. (See also *Anal. Abstr.*, 1957, **4**, 1786.) J. ŽYKA

1810. Colorimetric methods for the determination of phosphorus. E. Cadenas (Spanish Inst. Physiol. and Biochem., Madrid). *Inf. Quim. Anal.*, 1956, **10** (6), 209-215.—A review of the literature is presented, with 33 references. D. LEIGHTON

1811. Infra-red analysis of phosphorus compounds. D. E. C. Corbridge (Albright and Wilson Ltd., Oldbury, Birmingham, England). *J. Appl. Chem.*, 1956, **6** (10), 456-465.—A spectra-structure correlation chart for phosphorus compounds is presented, together with the existing evidence for such correlations. The use of data for the qualitative identification of powdered phosphate salts is discussed and examples are given of quantitative applications with the pressed disc technique. K. A. PROCTOR

1812. Simultaneous analyses by an ion-exchange method of phosphates, sulphates and chlorides. I. Behr (Israel Atomic Energy Commission). *Bull. Res. Council Israel*, A, 1956, **5**, 259-262.—Passage of a soln. containing PO_4^{3-} , SO_4^{2-} and Cl^- through a cationic exchanger (Amberlite IR-120) yields the corresponding acids. The total acid can be found by titration with 0.1 N NaOH to pH 8.98, the PO_4^{3-} by back-titration with 0.1 N HCl to pH 4.63, the Cl^- on a separate portion by AgNO_3 and the SO_4^{2-} by difference. A blank must be run on the distilled water. The mean error for about 80 tests was 0.7% for PO_4^{3-} , 4% for SO_4^{2-} and 1% for Cl^- . The same method has been used for soln. containing F^- in addition, the F^- being estimated on a separate portion. Three analyses can be made per day per column. G. BURGER

1813. Volumetric determination of hypophosphite in presence of phosphite by oxidation with ferric iron. M. N. Sastri and C. Kalidas (Andhra Univ., Waltair, S. India). *Rec. Trav. Chim. Pays-Bas*, 1956, **75** (9-10), 1122-1124 (in English).—A rapid volumetric method for the determination of hypophosphite, based on oxidation with Fe^{3+} and estimation of the Fe^{2+} formed, is described. Phosphite does not interfere. M. DAVIS

1814. Rapid analytical methods for metals and minerals. II. Determination of antimony in ores and concentrates. J. Doležal and P. Beran (Inst. Anal. Chem., Charles' Univ., Prague, Czechoslovakia). *Chem. Listy*, 1956, **50** (11), 1757-1760.—The interference due to Fe, Cu and As in the polarographic determination of Sb may be removed by means of hypophosphite. *Procedure*—To the finely powdered sample (1 g) in a 100-ml volumetric flask add conc. H_2SO_4 (5 ml) and heat to dissolve. Cool, add water (10 ml), make up to vol. with conc. HCl and allow the undissolved residue to settle. Measure 20 ml of this soln. into a 50-ml volumetric flask, add NaH_2PO_4 (1.2 g) and H_2O (5 ml) and set aside for 10 to 20 min (for the reduction of As). Make up to vol. with conc. HCl and set aside for 8 hr. Record the polarographic wave of a 5 to 10-ml aliquot from -0.15 to -0.35 V vs. the S.C.E. A comparison is made with the distillation and electrolytic methods. The procedure for the determination of Sb in ores containing Bi and high concn. of Cu is described, and a list of $E_{1/2}$ values for several metals in 8 N HCl is presented. J. ŽYKA

1815. Separation and detection of vanadium, molybdenum and titanium by capillary chromatography. P. Černý (Inst. Anal. Chem., Fac. of Sci., Bratislava, Czechoslovakia). *Chem. Listy*, 1956, **50** (12), 2026-2028.—Capillary chromatography can

be used for the separation of V, Mo and Ti, with a catechol reagent for their detection (to 1 g of catechol dissolved in a small vol. of H_2O add 3 ml of 20% Na_2SO_3 and 1 ml of conc. acetic acid, and dilute to 10 ml). The procedure is described and the influence of other elements discussed. J. ŽYKA

1816. Determination of oxygen in titanium, zirconium, chromium, vanadium and steels by bromination-carbon reduction method. M. Codell and G. Norwitz (Pitman-Dunn Lab., Frankford Arsenal, Philadelphia, Pa., U.S.A.). *Anal. Chem.*, 1956, **28** (12), 2006-2011.—The procedure described previously (*cf. Anal. Abstr.*, 1956, **3**, 94) has been modified to increase the accuracy and to extend the method to Zr (0.03 to 0.5% of O), Cr (0.1 to 0.5%), V (0.1 to 2%) and to steel containing >0.05% of O. The blank is considerably reduced by purifying the Br as described; the Cu in the purification train of the apparatus must be changed frequently. For Cr and V a temp. of 925° and intimate admixture of the C (preferably spectrographic graphite) with the crushed sample are necessary. The final copper oxide tube should be kept at 500° and the flow of He should be constant at 210 bubbles per min. A platinum boat is preferable to one of gold, and is obligatory for samples containing V. The results are in good agreement with those obtained by the vacuum-fusion method, especially for V. W. J. BAKER

1817. Fixation of sulphur dioxide as disulphito-mercurate (II) and subsequent colorimetric estimation. P. W. West and G. C. Gaeke (Louisiana State Univ., Baton Rouge, La., U.S.A.). *Anal. Chem.*, 1956, **28** (12), 1816-1819.—Concn. as low as 0.005 to 0.2 p.p.m. of SO_2 in air can be determined by aspirating 38.2 litres of air through 10 ml of 0.1 M sodium tetrachloromercurate^{II} in a fritted bubbler, whereby the stable, non-volatile disulphito-mercurate^{II} ion $[\text{Hg}(\text{SO}_3)_2]^{2-}$ is formed. One ml of 0.04% *p*-rosaniline hydrochloride (HCl-bleached) is then added, followed by 1 ml of 0.2% formaldehyde. After 30 min. the extinction of the red-violet colour is measured at 560 m μ , a blank on 10 ml of the sodium tetrachloromercurate^{II} being run concurrently. The concn. of SO_2 is read from a curve prepared by using standard soln. of NaHSO_3 in sodium tetrachloromercurate^{II}. Beer's law is valid up to $\approx 25 \mu\text{g}$ of SO_2 per 10 ml of soln.; NO_2 in concn. >2 p.p.m. interferes; any ppt. caused by sulphides should be removed by centrifuging. W. J. BAKER

1818. Determination of certain compounds of sulphur in solutions containing thiostannates. N. N. Sevryukov (M.I. Kalinin Moscow Inst. of Non-ferrous Metals and Gold). *Zavod. Lab.*, 1956, **22** (12), 1422-1425.—From the results of several titrations and gravimetric determinations carried out under different conditions, the contents of sulphide, polysulphide, sulphite, thiosulphate, sulphate, total S, NaOH and Sn in soln. containing thiostannates used in the electrolytic refining of tin are determined. G. S. SMITH

1819. Determination of silicon in tungsten alloys and ferrotungsten by the phospho-sulphate method. M. V. Babaev (Chelyabinsk Ferro-alloy Works). *Zavod. Lab.*, 1956, **22** (11), 1294-1296.—The method described by Pen'kova and Yakovlev (*Zavod. Lab.* 1950, **16**, 12) is unsatisfactory since complexes are formed with silicic acid which cause artificially low results for silicon content. G. S. SMITH

1820. **Polarographic determination of uranium in uranium minerals.** M. L. Borlera (Turin Polytech., Italy). *Ric. Sci.*, 1956, **26** (10), 3097-3107.—The U is determined polarographically in citric acid- H_2SO_4 soln. Owing to the disproportionation of the U^{5+} , the height of the reduction wave of the UO_2^{2+} is influenced by the concn. of the two acids. With 2 M citric acid, however, the concn. of the H_2SO_4 does not affect the first reduction stage. The procedure for treating a uranium ore and dealing with Fe and other impurities is described. A preliminary chromatographic treatment is necessary only for low-grade ores. L. A. O'NEILL

1821. **Salicylhydroxamic acid as an analytical reagent. II. Colorimetric estimation of uranium, molybdenum, vanadium and iron (III).** Ajit Sankar Bhaduri and Priyadarshan Ray (Indian Ass. for the Cultivation of Sci., Calcutta, India). *Z. anal. Chem.*, 1957, **154** (2), 103-113 (in English).—Salicylhydroxamic acid forms coloured complexes with U, V, Mo and Fe^{3+} . Vanadium may be determined in the presence of Mo and U; Fe interferes. The estimation of U or Mo in the presence of each other or of V is not possible. The vanadium complex is soluble in ethyl acetate thus affording separation from Mo and U, but not from Fe. The sensitivities are—U 0.1 μg , Mo 0.015 μg , V 0.017 μg , Fe 0.0125 μg . M. F. C. LADD

1822. **Brilliant yellow as adsorption indicator in argentimetric determination of halogens.** J. Oliveira Meditsch (Sch. of Engng. P. Alegre, Brazil). *Engenh. e Quím.*, 1956, **8** (3), 1-3.—Brilliant yellow was studied as an adsorption indicator in the titration of soln. of chloride, bromide and iodide with $AgNO_3$, and compared with K_2CrO_4 . Brilliant yellow in a soln. of dextrin was a satisfactory adsorption indicator in the argentimetric determination of chloride under relatively acid conditions ($N HNO_3$), and bromide in a neutral or acid medium ($\approx 0.1 N$ acidity), and iodide in neutral medium in soln. of concn. between 0.1 and 0.01 N. H. PRITCHARD

1823. **Direct spectrophotometric determination of small amounts of chloride.** P. W. West and H. Coll (Louisiana State Univ., Baton Rouge, La., U.S.A.). *Anal. Chem.*, 1956, **28** (12), 1834-1838.—Two alternative procedures, both based on the use of pure $Fe(ClO_4)_3$ and measurement of the extinction of a chloro complex of Fe^{3+} , are described for the determination of $>100 mg$ of Cl^- per litre. The first method has the advantages of low background, temp. independence and small interference from SO_4^{2-} , but the reagent $[0.14 M Fe(ClO_4)_3$ in $11.8 N HClO_4]$ must be stored under anhyd. conditions. The sample is added to the reagent in the absence of light, and the extinction is measured at 353 $m\mu$. The concn. of Cl^- should be between 1 and 12 mg per litre. In the second method, the reagent is $0.2 M Fe(ClO_4)_3$ in $5 N HClO_4$, and, after addition of the sample, the extinction is measured at 348 $m\mu$. The concn. of Cl^- should be between 4 and 40 mg per litre. Precautions to be observed, limitations and interferences (with corrections) are stated. Only the turbidimetric methods can be regarded as more sensitive. W. J. BAKER

1824. **Mercurimetric determination of chlorides in zinc electrolytes by a potentiometric method.** Z. I. Ivanova and P. N. Kovalenko (V. M. Molotov Rostov State Univ.). *Zavod. Lab.*, 1956, **22** (12), 1428-1429.—The chloride soln. is titrated with

$Hg(NO_3)_2$ soln., with Hg as the indicator electrode and a S.C.E. as comparison electrode. Titration is carried out to the appearance of a sharp potential jump. The minimum content of Cl^- that can be determined is 0.5 mg per litre. G. S. SMITH

1825. **Determination of iodine in oil drilling brines.** J. Yofe and R. Fueridi (The Standards Inst. of Israel, Tel Aviv). *Bull. Res. Council Israel*, A, 1956, **5**, 271-272.—A modification of the method of Parker and Southwell (*Science of Petroleum*, 1938, **1**, 650; *J. Instn. Petrol. Tech.*, 1929, **15**, 138) was used to determine iodine in brine from drillings at Beeri. The sample (300 to 500 ml) was filtered, hydrocarbons were extracted with ether, and Ca and Mg removed by pptn. with Na_2CO_3 . The sample was concentrated on a water bath until NaCl began to crystallise. The crystals were redissolved and the soln. made up to 100 ml. An aliquot containing 0.5 to 1 mg of iodine was acidified to methyl orange with H_2SO_4 in a separating funnel. The iodine was liberated by addition of 5% H_2O_2 (0.5 to 1 ml) and extracted with CCl_4 for spectrophotometric determination at 500 $m\mu$. Under these conditions bromine is not liberated and all the iodine can be extracted. As little as 0.06 mg of iodine can be determined. G. BURGER

1826. **Chelatometry. XII. "Entametric" determination of manganese.** P. Wehber (Lab. Metallhütte Mark A.-G., Hamburg-Wilhelmsburg, Germany). *Z. anal. Chem.*, 1957, **154** (2), 122-124.—A soln. of Mn^{2+} , buffered at pH ≈ 8 by aq. NH_3-NH_4Cl , can be titrated with 0.1 M EDTA. Eriochrome black T or Eriochrome red B may be used as indicator. With 5.5 to 54.9 mg of Mn, the mean error was $\approx 0.4\%$. M. F. C. LADD

1827. **Photometric method for the determination of iron by means of a tri-*n*-butylammonium salt and 8-hydroxy-7-iodoquinoline-5-sulphonic acid (feron).** M. Ziegler, O. Glemser and N. Petri (Anorg.-chem. Inst., Univ. Göttingen, Germany). *Z. anal. Chem.*, 1957, **154** (3), 170-182.—If the acid hydrogen atoms, or their alkali derivatives, of certain metal complexes are replaceable by substituted ammonium residues, then the resulting metal complex is less soluble in water than the original complex, and may be extracted from the aq. phase. As a result the sensitivity and specificity of the reaction are increased. Further, the colour reaction is less dependent on the pH of the solution. As an example, the Fe^{3+} -tri-*n*-butylammonium-feron complex may be readily extracted from a weakly acid medium with isoamyl alcohol. The spectrum of the isoamyl alcoholic soln. of this complex showed absorption maxima at 370, 465 and 610 $m\mu$. Comparison with the spectrum of tri-*n*-butylammonium-feron indicated that the maximum at 610 $m\mu$ could be used without interference from co-extracted reagent. The extinction was constant over the pH range 2.5 to 7.5. *Procedure*—The test soln. (25 to 50 ml), containing up to 150 μg of Fe^{3+} , is buffered to a pH of 4.7 with Na acetate-acetic acid and shaken, first with 0.1% aq. feron soln. (4 ml) and then with tri-*n*-butylammonium acetate (1 to 2 ml). The complex formed is extracted with isoamyl alcohol (5 ml). The extract is made up to 10 ml with isoamyl alcohol washings. The absorption is measured at 610 $m\mu$. A calibration curve shows that Beer's law is obeyed. Interferences by other ions are discussed. L. S. ADLER

1828. Coulometry with quinquivalent uranium. Determination of ferric ion. K. W. Edwards and D. M. Kern (Dartmouth Coll., Hanover, N.H., U.S.A.). *Anal. Chem.*, 1956, **28** (12), 1876-1878.—From 0.025 to 25 mg of Fe^{3+} can be titrated coulometrically, at pH 1.5 to 2.5 (HCl), with U^{5+} generated internally from uranyl soln. and having a standard potential of -0.06 V vs. the S.C.E. The generating soln. ($\approx 0.02 \text{ M}$ UO_2^{2+} for c.d. $\geq 0.5 \text{ mA}$ and $\approx 0.1 \text{ M}$ for c.d. of 2.5 mA) and the sample soln. are de-aerated for 15 min. with N_2 ; the titration time is $\approx 500 \text{ sec.}$, bubbling of N_2 and measurement of indicator current proceeding continuously. About 0.3 V is applied across two platinum-gauze electrodes. Provided that mixing is efficient, the end-point is sharp. The error is within $\pm 0.2\%$; the decomposition of U^{5+} into U^{4+} and U^{6+} does not cause interference, but if NO_3^- are present the results are slightly high.

W. J. BAKER

1829. Triphenylmethane dyes as compleximetric indicators for the determination of iron. L. Sommer and Z. Kolářik (Inst. Anal. Chem., Masaryk Univ., Brno, Czechoslovakia). *Chem. Listy*, 1956, **50** (9), 1445-1449.—Various derivatives of triphenylmethane and trinaphthylmethane dyes were studied as indicators for the compleximetric determination of iron, and Eriochrome cyanine R was found to be the most suitable.

J. ŽÝKA

1830. The photometric estimation of iron with tributylammonium hexathiocyanatoferrate (III). M. Ziegler, O. Glemser and N. Petri (Anorg.-chem. Inst. der Univ., Göttingen, Germany). *Z. anal. Chem.*, 1957, **154** (2), 81-98.—Tributylammonium hexathiocyanatoferrate $[\text{HN}(\text{C}_4\text{H}_9)_3]_3[\text{Fe}(\text{SCN})_6]$ has been used for estimating Fe^{3+} in the ranges 0.1 to $1.5 \mu\text{g}$ and 1 to $20 \mu\text{g}$. The concn. limit is stated to be 1 in 150×10^6 . The effect of the presence of several different cations was studied and the specificities attained in the determination of $2 \mu\text{g}$ of iron ranged from $\text{Fe}^{3+}:\text{Sn}^{4+} = 1:800$ to $\text{Fe}^{3+}:\text{Al}^{3+} = 1:10^6$.

M. F. C. LADD

1831. The determination of iron in iron ores, slags and refractories by thioacetamide reduction. P. H. Scholes (B.I.S.R.A., Metallurgy (Gen.) Div. Lab., Hoyle St., Sheffield, England). *Analyst*, 1956, **81**, 688-693.—In the method described, thioacetamide is used to produce H_2S by hydrolysis *in situ* in the test soln. and the use of the gas is thus avoided. The sample (0.5 g) is dissolved in conc. HCl and the soln. is evaporated to fuming with dil. H_2SO_4 . After dilution and heating, the liquid is oxidised with a slight excess of KMnO_4 soln. and, after further dilution, the mixture is boiled and treated with a suitable amount of aq. 1% thioacetamide soln. and boiling is continued for 20 min. The pptd. sulphides are collected on paper pulp and washed with dil. H_2SO_4 . The filtrate is treated with a specified amount of dil. H_2SO_4 , boiled for 30 min., and diluted to $\approx 450 \text{ ml}$; 0.5 ml of ferroin indicator (prep. described) is added and the mixture is titrated with 0.1 N ceric sulphate. A reagent blank should not exceed 0.05 ml of the titrant. Modifications of some details are noted for certain types of sample. Under the specified conditions of acidity, V does not interfere. If Cr^{6+} are formed during the procedure they must be reduced before addition of thioacetamide, or additional thioacetamide must be added to effect the reduction.

A. O. JONES

1832. Flame-spectrophotometric determination of copper in ferrous alloys. J. A. Dean and J. H. Lady (Univ. of Tennessee, Knoxville, U.S.A.). *Anal.*

Chem., 1956, **28** (12), 1887-1889.—From 0.01 to 1% of Cu in a wide range of ferrous alloys can be determined by flame spectrometry of the salicylaldehyde complex, which can be selectively extracted with either CHCl_3 or n -amyl acetate from a soln. of the sample at pH 3 (citrate buffer). The extract is aspirated directly into an oxy-acetylene flame, thereby avoiding interference from other elements (as in a bulk sample) and increasing the spectral emission of the Cu $324.7\text{-m}\mu$ line tenfold in comparison with an aq. soln. of Cu . The lower limit of accurate measurement is $0.5 \mu\text{g}$ of Cu per ml .

W. J. BAKER

1833. Theoretical bases of the determination of the carbide phase in carbon steel. Yu. A. Klyachko and O. D. Larina (Central Sci. Res. Inst. of Ferrous Metall.). *Zavod. Lab.*, 1956, **22** (12), 1409-1415.—Experiments on the electrochemical phase analysis of carbon steel (0.65% of C) are carried out for the purpose of studying the effects of c.d., temp., and other factors.

G. S. SMITH

1834. Boron determination in steel. R. Suárez Acosta. *Inst. Hierro y Acero*, 1956, **9**, 70-74.—For this colorimetric method, dissolve 1 g of steel in 20 ml of 7 N H_2SO_4 ($1:4$) in a 50-ml Erlenmeyer flask (free from B), at 60° . Cool, and filter into a calibrated bottle. Since the residue may contain B , fuse it with Na_2CO_3 , dissolve the melt, and add the soln. to the filtrate. If the soln. is turbid add a few drops of H_2SO_4 . Add 2 to 3 ml of H_2SO_4 , heat in a closed bottle to 40° until the soln. is colourless; cool and make up to the calibration mark. Remove 5 ml of soln., and in a 30-ml test-tube add carefully 20 ml of conc. H_2SO_4 , then 1 ml of quinalizarin. Close the tube, mix the contents carefully, heat again for 20 to 30 min. until the colour is well developed, and cool. Measure the extinction, with orange filter No. 607, and compare with a calibration curve. The method is suitable for the determination of 0.001 to 0.004% of B in steel.

CHEM. ABSTR.

1835. Determination of rare earths in steel. H. Krapp. *Arch. Eisenhüttenw.*, 1956, **27**, 103-105.—The customary fluoride, peroxide and oxalic acid methods do not give exact results and were modified so that the content of rare earths in steels with high chromium and nickel contents ($\text{Cr } 35$, $\text{Ni } 20$ and $\text{C } 0.1\%$) can be determined accurately, independent of the valency in which Fe is bound. Aqua regia is used to dissolve 2 g of the sample, and the rare earths are then converted into sulphates, chlorates or chlorides; for the separation of the rare earths, ion exchangers are used. The different procedures are described.

CHEM. ABSTR.

1836. Potentiometric determination of vanadium in steels rich in chromium. J. Bünger (Edelstahlwerke, Berghausen, Cologne, Germany). *Arch. Eisenhüttenw.*, 1955, **26**, 675-678.—Because of the difficulty of visual detection of the end-point in the volumetric determination of low vanadium contents in the presence of high chromium contents, the applicability of the potentiometric method of Thanheiser and Dickens (*Arch. Eisenhüttenw.*, 1931-32, **5**, 105) was investigated. An additional difficulty with the volumetric method in the presence of $>10\%$ of Cr is that addition of increased excess of KMnO_4 results in the oxidation of progressively more Cr . The potentiometric method offers a reliable and rapid method for the determination of V in the range 0.04 to 2.7% in Cr -rich steels. Procedure—Dissolve 0.5 g of steel turnings in a

300-ml Erlenmeyer flask with 100 ml of acid mixture (700 ml of water, 100 ml of conc. H_3PO_4 and 200 ml of conc. H_2SO_4). If HCl and HNO_3 are necessary to effect dissolution of the steel, add only 50 ml of H_3PO_4 - H_2SO_4 mixture and evaporate to fumes. Then after slight cooling dissolve the residue in the remaining 50 ml of acid mixture diluted with water. Add KMnO_4 soln. (2.5%) until an intense red coloration is formed and heat for 2 min. Add solid FeSO_4 until the permanganate colour disappears and there is no further change in the colour of the clear soln. Cool to $<30^\circ$ and run in KMnO_4 soln. (2.5%) until a pale-red colour persists for 1 min., then add an excess of 2 to 3 drops. Add approx. 2 g of urea and NaNO_2 soln. (3%) dropwise until the permanganate colour disappears and an excess of 5 to 10 drops is present. Titrate potentiometrically with 0.02 N ferrous ammonium sulphate. The titre is determined against a normal steel, or against a standard vanadium soln.

D. F. PHILLIPS

1837. Photometric determination of molybdenum in steel. J. Bünger (Edelstahlwerke, Berghausen, Cologne, Germany). *Arch. Eisenhüttenw.*, 1955, **26**, 333-335.—A direct and rapid method is described for the determination of 0.2 to 5% of Mo in steel. This depends on measurement of the extinction of the molybdenum thiocyanate complex after reduction with SnCl_2 . *Procedure*—Dissolve 0.5 g of steel turnings in 30 ml of H_3PO_4 - H_2SO_4 mixture (150 ml of conc. H_3PO_4 and 150 ml of conc. H_2SO_4 diluted to 1 litre with water). Oxidise with conc. HNO_3 and evaporate to fuming. Dissolve the residue in water and dilute to 250 ml. If the steel is insol. in the acid mixture described, use equal parts of conc. HCl, conc. HNO_3 and water followed by 30 ml of the H_3PO_4 - H_2SO_4 mixture and evaporate to fumes. To a 10-ml portion of the soln. add successively (shaking after each addition) 20 ml of H_2SO_4 - HNO_3 mixture (100 ml of conc. H_2SO_4 and 50 ml of conc. HNO_3 diluted to 1 litre), 10 ml of 10% NH_4SCN soln. and 10 ml of SnCl_2 soln. Measure the extinction after 5 min. against water, with the filament lamp of a Pulfrich photometer and filter S53. The colour remains almost stable for 2 hr. Straight-line calibration graphs are obtained which pass through the origin. For amounts of Mo $<0.2\%$, add H_2SO_4 - HNO_3 mixture containing 2 mg of Mo per litre in order to adjust the extinction of a layer 5 cm thick to 0.23. For molybdenum contents of $>5\%$, correspondingly smaller sample weights should be taken. Interference from other elements is slight. The error for 2% of Mo is $\pm 0.03\%$.

D. F. PHILLIPS

1838. Colorimetric determination of cobalt with furil α -monoxime. J. Martinek and V. Hovorka (Inst. Anal. Chem., Vysoká škola chemická, Prague, Czechoslovakia). *Chem. Listy*, 1956, **50** (9), 1450-1455.—Furil α -monoxime (I) (preparation described) reacts with cobaltous salts to form a red-orange complex, stable in acid soln. The complex can be extracted into organic solvents and used for the colorimetric determination of 1 to 200 μg of Co. *Procedure*—Neutralise the soln. of the sample containing 1 to 200 μg of Co (if Ni and Cu are present, only 1 to 100 μg of Co) with KOH soln. (5%) and adjust to a pH of 5 to 6. Add a saturated soln. of NaF (20 ml) for masking Fe^{3+} and Al^{3+} and a soln. of I in pyridine (10%) (5 ml) and set aside for 10 min. Add HCl (1:1) (15 to 20 ml) and extract with pure CHCl_3 (2 \times 12 ml). Place the extract in a 25-ml volumetric flask, remove the turbidity by adding

pyridine (1 ml), make up to vol. with CHCl_3 and measure the extinction at 395 to 415 $m\mu$. This method was used with excellent results for the determination of Co in steel, technical nickel and pyrrhotites.

J. ŽÝKA

1839. Determination of cobalt and nickel in manganese ores and slags, using ethylxanthate. A. T. Pilipenko and V. A. Bogolyubskii (Kiev Univ., Ukr. SSR). *Ukrain. Khim. Zhur.*, 1956, **22** (1), 97-99.—A sample of ore containing 0.03 to 1 mg of Co is digested with conc. HCl, and the soln. is evaporated down to small vol. and filtered from the SiO_2 . The filtrate is diluted to ≈ 40 ml, an excess of M K ethylxanthate is added, and heavy-metal xanthates are extracted with CCl_4 . The extract is shaken with ammoniacal tartrate, the Co xanthate content of the CCl_4 layer is determined colorimetrically, and the Ni content of the aq. tartrate layer by the dimethylglyoxime method. The same procedure is applicable to slags, after treatment with aqua regia.

R. TRUSCÖE

1840. Spectrophotometric method for simultaneous determination of nickel and cobalt. R. D. Whealy and S. O. Colgate (West Texas State Coll., Canyon, U.S.A.). *Anal. Chem.*, 1956, **28** (12), 1897-1898.—Aqueous soln. of nickelous and cobaltous nitrates react completely with diethylenetriamine to form sol. coloured complexes, the light-absorption properties of which can be used for the quant. determination of both Ni and Co in the absence of interfering cations (Cu, Cr, Mn). Beer's law is followed closely for concn. of Ni of 0.01 to 0.06 g-ion per litre and a concn. of Co of 0.001 to 0.006 g-ion per litre. Deviations from standard values are $\pm 5\%$ for Ni and $\pm 10\%$ for Co.

K. A. PROCTOR

1841. The reaction of phthalimide oxime with bivalent nickel salts. A. Okáč and J. Horák (Inst. Anal. Chem., Masaryk Univ., Brno, Czechoslovakia). *Chem. Listy*, 1956, **50** (9), 1496-1497.—In a soln. of pH 7.3, phthalimide oxime (I) reacts with bivalent nickel ammonium salts, yielding a yellow, crystalline compound ($\text{C}_8\text{H}_4\text{O}_2\text{N}_2\text{Ni}$); in low concn. a yellow colloidal soln. is obtained. This reaction can be used for a sensitive detection of Ni^{2+} . *Procedure*—To a neutral soln. of the sample add an ethanolic soln. of I (0.5%) (1 ml) and aq. NH_3 (10%) (one drop). Ions that form hydroxides in slightly alkaline medium must be first pptd. with aq. NH_3 and the reaction must be carried out in the neutralised soln. of the ammonium salts. Interference is caused by Cu^{2+} and Co^{2+} ; Cu can be removed with KSCN and sulphate; when Co is present, the reagent must first be added to a neutral soln. of the sample, followed by aq. NH_3 .

J. ŽÝKA

1842. Spectrographic determination of nickel, copper, iron, manganese and silicon in metallic cobalt. P. M. Mikhailov and O. Ch. Velichko ("Severonikel" Combine). *Zavod. Lab.*, 1956, **22** (11), 1307-1310.—The methods of obtaining a sample and the conditions for spectrographic analysis in an a.c. arc of Ni, Cu, Fe, Mn and Si in metallic cobalt are described.

G. S. SMITH

1843. The chromatographic separation of nitrate complexes of nitrosylruthenium in nitric acid solution. A. G. Wain, P. G. M. Brown and J. M. Fletcher (Chem. Div., A.E.R.E., Harwell, England). *Chem. & Ind.*, 1957, (1), 18-20.—Ruthenium distribution measurements with different relative volumes (cf. Martin and Gillies, A.E.R.E. C/R 816,

1951) of the solvent phase [kerosene-diluted tributyl phosphate (TBP)] and of the aq. phase have been used to determine the compositions of synthetic solutions ($\approx 10^{-3}$ M Ru) of nitrate nitrosyl-ruthenium complexes at equilibrium in HNO_3 , and to calculate the individual partition coefficients (K) for the nitrate complexes extracted by TBP. The results are given. The same solutions of nitrate nitrosylruthenium complexes have been examined by paper chromatography by applying 0.01 ml of a soln. containing $>10^4$ γ counts per min. per ml of ^{106}Ru to a Whatman CRL/1 paper strip, and eluting upwards with methyl isopropyl ketone made 1.1 M in HNO_3 by exhaustive equilibration with 3 M HNO_3 . Histograms derived from counting 0.5-cm sections of the paper strip, divided after rapid air-drying, indicate (i) good resolution of the trinitrate complex; (ii) a separation of the di- and mono-nitrate complexes, but with appreciable tailing of each; and (iii) the presence of polynuclear species ($R_F < 0.1$) in 3 M HNO_3 , but their absence in 7.5 M HNO_3 . The values for R_F and K (determined for 3 M HNO_3 and equilibrated methyl isopropyl ketone) for the mono-, di- and tri-nitrate (RuNO) complexes and uranyl nitrate are given and discussed. This type of chromatography has been used (a) to estimate the compositions of solutions of these nitrate complexes; (b) to estimate, by γ counting, the percentage of Ru present as the trinitrate complex in freshly dissolved or in processed solutions of irradiated U; and (c) to determine the courses and rates of reactions by which (RuNO) nitrate complexes are converted into nitro complexes in the presence of HNO_3 . O. M. WHITTON

1844. Analytical chemistry of the platinum metals. IV. The spectrophotometric estimation of osmium with tetraphenylarsonium chloride. R. Neeb (Anorg.-chem. Inst. der Univ., Mainz). *Z. anal. Chem.*, 1957, **154** (1), 23-26.—A conc. HCl soln. of Os^{4+} forms a yellow ppt. with tetraphenylarsonium chloride, which may be dissolved in CHCl_3 and estimated colorimetrically. The presence of ruthenium up to 200-fold excess does not cause interference. M. F. C. LADD

1845. Analytical chemistry of the platinum metals. III. The spectrophotometric determination of iridium with tetraphenylphosphonium bromide. R. Neeb (Anorg.-chem. Inst. der Univ., Mainz). *Z. anal. Chem.*, 1957, **154** (1), 17-22.—Small amounts of Ir have been determined with tetraphenylphosphonium bromide. Other platinum metals, except Rh, interfere. For quantities of Ir between 30 and 150 μg the mean error was $\approx 2\%$. For ratios of Rh to Ir of (15 to 30):1 and quantities of Ir between 30 and 140 μg the mean error was again $\approx 2\%$. M. F. C. LADD

1846. The determination of impurities in steam. C. Janssen and G. B. Smit (KEMA Lab., Arnhem, Netherlands). *J. Appl. Chem.*, 1956, **6** (11), 516-524.—A suitable conductivity method for the determination of low salt contents in steam condensates is described. The interference caused by NH_3 and CO_2 can be completely eliminated by degassing. A formula is given for converting conductivity to total dissolved solids, in p.p.m. K. A. PROCTOR

1847. Analysis of fluxes for magnesium casting by a spectrographic method. M. Ya. Patrín and N. I. Kulýgina. *Zavod. Lab.*, 1956, **22** (11), 1318-1319.—The flux itself and the portion insoluble in water (CaF_2 and MgO) are analysed separately by a.c. arc excitation of the powders on a carbon

electrode. Two relevant sets of standards, each containing CuCl_2 to give Cu as an internal standard, are prepared. G. S. SMITH

1848. Spectrographic analysis of agglomerates. I. K. Malboroda and I. N. Treiger ("Zaporozhstal" Works). *Zavod. Lab.*, 1956, **22** (11), 1312-1313.—The determination of Mn, Mg and Al in agglomerates, ores and slags is carried out by fusing the sample with Na_2O_2 , dissolving the melt in HCl , introducing $(\text{NH}_4)_2\text{MoO}_4$ as an internal standard and exciting the soln. in a fulgurator of special type (illustrated) between carbon electrodes. G. S. SMITH

1849. Simultaneous determination of water and total carbon dioxide in phosphorites. A. Jęczalik (Geological Inst., Warsaw). *Chem. Anal., Warsaw*, 1956, **1** (1), 35-52.—The determination of chemically combined water (volatilised at over 110°) in phosphorites is difficult owing to the presence of fluorine, and the fact that the apatite structure is stable even at high temp. It is therefore impossible to use the conventional methods applied to rocks and minerals which are based on heating the sample in a tube at about 1000° . In the technique described, sodium tungstate is used as flux and magnesium oxide as absorbent for fluorine. The fusion is carried out in an ordinary-glass tube, with a bulb, shielded with a piece of platinum foil only at the point where it is heated. The estimation can be carried out at the relatively low temp. of 700° . *Procedure*—In the straight part of a fusion tube place a layer of MgO about 3 cm long (to absorb the volatile compounds of F, Cl and S) between two plugs of glass-wool. Connect the tube with an air-purifying train (KOH soln., soda-lime, CaCl_2 , P_2O_5). Heat the tube, the absorbent and the glass-wool plugs with a burner to a red heat and pass a slow stream of air for about 10 min. Allow to cool. Weigh 0.5000 g of the sample and 3.5 g of the flux and, if no free silica is present in the sample, add 0.2 g of finely powdered quartz. Transfer the mixture to the bulb of the fusion tube and add another 0.4 g of the flux. Stopper the tube with glass-wool and place it inside a metal box serving as a drying chamber. Pass a slow stream of purified air and heat at 110° for 30 min. to remove hygroscopic water from the sample. Cool, remove the drying chamber and attach weighed absorption vessels for H_2O (anhyd. CaCl_2 and P_2O_5 , satd. with CO_2) and for CO_2 (KOH soln.). Cover the bulb with a piece of platinum foil and, passing a slow stream of air, heat with a burner until the mixture melts (about 700°). Heat for 30 min. then cool to room temperature and weigh the absorption vessels. Carry out a blank determination exactly as described above. The accuracy of results is within $\pm 3\%$ for H_2O and $\pm 0.5\%$ for CO_2 ; the time required for a determination is 70 min. K. F. SPOREK

1850. Mass-spectrometer analysis of gases in blisters in glass. B. J. Todd. *Trans. Soc. Glass Tech.*, 1956, **40**, 327-387.—Details are given of the collection of gas from the blisters, the determination of its quantity by allowing it to expand to a known vol., where its pressure is measured with a Pirani gauge, and its chemical analysis by condensation (H_2O is condensed at -78.5° ; CO_2 and SO_2 are not condensed at -78.5° , but are at -196° ; and O, N, CO, A, and H are not condensed at -196°) and with a G.E. Model 8665934-GI mass spectrometer. Typical analyses are (i) O 91 to 98, N 8 to 1%; (ii) N 98, A 1%; and (iii) CO_2 97, N 3%. J. A. SUGDEN

1851. **Identification of inorganic fibres.** W. Bobeth and U. Müller (Inst. for Text. Tech., Tech. High School, Dresden). *Faserforsch. u. Textiltech.*, 1956, 7 (11), 497–504.—Rapid and reliable microchemical methods are devised for identifying slag fibres (I), mineral fibres (e.g., sillan and basalt) (II), ceramic fibres (Fiberfrax) (III), glass fibres (IV), quartz fibres (V) and asbestos fibres (VI). In a systematic analysis, described and illustrated, the sample fibre, freed from lubricants and dressing, is treated successively with the following reagents with the results indicated—(i) 2% H_2SO_4 , I dissolves with formation of CaSO_4 crystals; (ii) 37% H_2SO_4 , II dissolves with formation of CaSO_4 crystals; (iii) a mixture (1:1) of 37% H_2SO_4 and 10% HF, both III and IV dissolve, III without residue and IV with formation of crystals or a granular residue; (iv) a mixture (4:1) of 20% HF and 5% $\text{K}_4\text{Fe}(\text{CN})_6$, both V and VI remain undissolved; V remains uncoloured, but VI becomes blue or green according to type, and VI has a characteristic structure. Supplementary tests include (a) treatment with a mixture (1:3:5) of 15% HCl and 5% $\text{K}_4\text{Fe}(\text{CN})_6$ solution to distinguish between different types of slag and mineral fibres (by characteristic colour formation), (b) treatment with a mixture (2:1) of 17% H_2SO_4 and 10% HF to distinguish between sillan and basalt (both dissolve, but sillan shows crystal growth), (c) treatment with a mixture (1:1) of 37% H_2SO_4 and 10% HF to distinguish between high-alkali, low-alkali and calcium glasses (by type and amount of crystal formation), and (d) treatments with 40% HF, or KI solution (1:9), or a mixture (4:1) of 20% HF and 5% $\text{K}_4\text{Fe}(\text{CN})_6$ solution, to distinguish between different types of asbestos. Means are described for avoiding corrosion of the object glasses when HF reagents are used.

H. L. WHITEHEAD

1852. **Determination of organic impurities on the surface of metal parts by a spectrographic method.** R. N. Rubinshtein and N. G. Karpel. *Zavod. Lab.*, 1956, 22 (11), 1327–1330.—The method is designed for the determination of grease, etc., on small (≈ 1 sq. cm) surfaces. The object in a discharge tube containing He at a pressure of 10 mm is placed in the field of a high-frequency discharge and the spectrum is photographed during 5 min. The lines CH 4312.5, C 4737.1, C 4102.3, H 4861.3 and H 6562.8 Å are measured relatively to the line He 4921.9 Å.

G. S. SMITH

See also Abstracts 1739, 1742, 1743, 1744, 1749, 1751, 1755, 1858, 1876, 1915, 1916, 1917, 1980, 1992, 1993, 1994, 1995, 2030, 2031, 2046.

3.—ORGANIC ANALYSIS

1853. **Körbl's method of catalytic combustion of organic compounds.** A. Okáč and M. Vrchlábský (Inst. Anal. Chem., Masaryk Univ., Brno, Czechoslovakia). *Chem. Listy*, 1956, 50 (12), 2042–2043.—By analysing a variety of organic compounds, and by a comparison with other procedures, it has been found that Körbl's method of catalytic combustion (*Chem. Listy*, 1955, 49, 858, 862, 929, 1532, 1664) is an excellent and simple method for qualitative and quantitative elementary organic analysis. The possibilities of some minor improvements are discussed.

J. ZÝKA

1854. **Recent developments in quantitative organic elementary analysis. I. Carbon, hydrogen and oxygen.** G. Kainz (II Chem. Lab., Univ. Vienna).

Öst. ChemZtg, 1956, 57 (15–16), 216–221.—A review is presented covering improvements in balances, advances in oxidation procedure, removal of interfering impurities and the estimation of the products. For the complete oxidation of difficultly combustible materials a variety of catalysts has been tried and temp. up to 1000° are used. Attention is given to the removal of N and fluorides. Absorbents for H_2O and CO_2 are discussed. An isotope-dilution method has been used for the estimation of O. (67 references.)

G. BURGER

1855. **Causes of error in the micro-determination of nitrogen by Kjeldahl, followed by nesslerisation.** J. González Carrero, O. Carballido Ramallo and F. Gómez Vigide ("Alonso Barba" Inst. Chem., Univ. Santiago de Compostela, Spain). *Inf. Quim. Anal.*, 1956, 10 (6), 199–208.—The literature is cited and experimental analyses are described that show that only ammoniacal N is determined by nesslerisation, which does not detect the organic amines and other nitrogen compounds produced in the original Kjeldahl treatment.

D. LEIGHTON

1856. **Semi-micro Kjeldahl determination of nitro and amido nitrogen. I. Selenium catalysts.** A. Takeda and J. Senda. *Ber. Ohara Inst.*, 1956, 10 (4), 241–244.—Satisfactory results in the semi-micro determination of nitro and amido nitrogen by the Kjeldahl method were obtained with the following catalyst mixtures—(i) anhyd. K_2SO_4 (1 g), metallic Se (15 mg) and yellow HgO (70 mg); (ii) mixture (i) with 20 mg of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$; and (iii) mixture (i) without the HgO . Approx. 1 g of each catalyst is used with a sample containing ≈ 5 mg of N.

S.C.I. ABSTR.

1857. **Organic quantitative analysis. VIII. Micro-estimation of sulphur in organic compounds. Mechanism of formation of silver sulphate.** M. Večeřa and D. Šnobl (Res. Inst. Org. Synth., Pardubice-Rybitví, Czechoslovakia). *Chem. Listy*, 1956, 50 (12), 1941–1947.—The formation of Ag_2O on the surface of silver in an atmosphere of O, even at temp. $> 300^\circ$, has been suggested as a basis for the mechanism of the reactions of sulphur oxides with silver. The following conditions for the micro-estimation of sulphur via Ag_2SO_4 have been found to be most suitable—temp. 450° , silver surface 2.3 sq. dm, combustion time about 20 min. and velocity of the oxygen stream 10 to 20 ml per min.

J. ZÝKA

1858. **Determination of silicon in organosilicon compounds.** A. P. Kreshkov, S. V. Syavtsillo and V. T. Shemyatenkova. *Zavod. Lab.*, 1956, 22 (12), 1425–1427.—Decomposition is effected in a weighed quartz flask with a mixture of 25% oleum and fuming HNO_3 containing 20% of oxides of N. The heated mixture is treated with further amounts of fuming HNO_3 until decomposition is complete, the acids are evaporated off and the flask containing the residue of SiO_2 is weighed.

G. S. SMITH

1859. **New modification of the semi-micro determination of the acetyl group.** B. Buděšinský (Res. Inst. Pharm. and Biochem., Prague, Czechoslovakia). *Chem. Listy*, 1956, 50 (12), 1936–1940.—An automatic apparatus for the distillation of acetic acid, produced when determining acetyl groups by hydrolysis of acetylated compounds with H_2SO_4 , was constructed. The accuracy of this method is compared with that in which the partial distillation is compensated by the titration error, caused by the presence of SO_4 formed in hydrolysis. The method

of quant. distillation yields better results and was tested by analysing 16 different acetyl compounds. The procedure and apparatus are described.

J. ŽYKA

1860. Standard-substance technique for the characterisation of organic compounds by gas chromatography. E. Kováts and E. Heilbronner (Edwig. Tech. Hochschule, Zurich, Switzerland). *Chimia*, 1956, **10**, 288-289.—*n*-Decane is used as a standard in the work described, for which simple theory is given. It is shown that the addition of one methylene group to the length of the chain has the same effect on the pV value of a primary normal alcohol as on that of a normal paraffin. E. G. CUMMINS

1861. Analysis of hydrocarbon gases by the chromatothermographic method. E. I. Svetsitskii, N. I. Lulova, A. I. Tarasov and E. I. Zemskova. *Zavod. Lab.*, 1956, **22** (12), 1399-1403.—The apparatus is a modification of that described by Turkel'taub (*Zhur. Fiz. Khim.*, 1953, **27**, 1827). The sample from a gas-measuring burette is passed into the top of a silica-gel column which is fitted with an electric furnace that can be moved down the length of the column by means of a motor. Air is passed through the column and the desorbed hydrocarbons and air are passed through ascarite and then into a combustion furnace and further into a gas-analysis apparatus. The individual saturated and unsaturated hydrocarbons from C_1 to C_4 in a mixture can be determined, the results being automatically registered. The error is normally within $\pm 1.5\%$ of the vol. of the sample. G. S. SMITH

1862. Chromatographic analysis of saturated hydrocarbons C_3 - C_7 on natural sorbents. T. G. Andronikashvili and L. P. Kuz'mina (Inst. of Petroleum, Acad. Sci., U.S.S.R.). *Zavod. Lab.*, 1956, **22** (12), 1403-1406.—The use of natrolite, tripoli, diatomite and kaolin as adsorbents in chromatograph columns at 100° to 180° is described. G. S. SMITH

1863. Determination of alcohols in aqueous ethanol-*i*sopropyl alcohol mixtures. F. Strache and E. Martienssen (Chem. und Lebensmitteluntersuch. des Hyg. Inst. der Hansestadt, Hamburg, Germany). *Z. Lebensmitt. Unters.*, 1956, **104** (5), 339-344.—The method described is based on the measurement of the density of the mixture (giving the total alcohols) and oxidimetric determination of ethanol. Mathematical and graphical treatments of the analytical results are presented. Test analyses indicating the limit of error of the method are given. S.C.I. ABSTR.

1864. Determination of sugars on paper chromatograms with *p*-anisidine hydrochloride. J. B. Pridham (Inst. of Paper Chem., Appleton, Wis., U.S.A.). *Anal. Chem.*, 1956, **28** (12), 1967-1968.—The sugar soln. is applied to the chromatographic paper as small discrete spots and, after development and drying, the strip is sprayed with *p*-anisidine hydrochloride reagent and heated at 130° . The resulting coloured spots and suitable blanks are cut from the paper and are extracted into a methanol- SnCl_2 soln. The extinctions are measured at $510\text{ m}\mu$ for aldopentoses and hexuronic acids, at $400\text{ m}\mu$ for aldohexoses, and at $385\text{ m}\mu$ for 6-deoxyaldohexoses. The recovery of total sugar from a hydrolysate was 99%. The concn. range is 5 to $50\text{ }\mu\text{g}$. G. P. COOK

1865. Spectrophotometric method for determination of sugars. T. E. Timell, C. P. J. Glaudemans and A. L. Currie (McGill Univ., Montreal, Que., Canada). *Anal. Chem.*, 1956, **28** (12), 1916-1920.—The method is based on the colour developed by aldopentoses, aldohexoses, methylaldopentoses, hexuronic acids, certain oligosaccharides and methylated monosaccharides with an acetic acid soln. of *o*-aminodiphenyl. Beer's law is followed over the concn. range 20 to $500\text{ }\mu\text{g}$ per ml, and both the colour and the reagent are sufficiently stable; the absorption max. for all sugars tested lay in the $380\text{-m}\mu$ region. Individual reference curves for the different sugars are needed, although in some instances absorbances are identical for several sugars. A probable error of $\pm 4\%$ was obtained in the determination of glucose at concn. below $100\text{ }\mu\text{g}$ per ml, and $\pm 1\%$ at higher concn. The method was found to be useful in conjunction with paper chromatography. G. P. COOK

1866. Colorimetric determination of fructose with indol-3-ylacetic acid. A. Heyrovský (Intern. Hosp., Charles' Univ., Prague, Czechoslovakia). *Chem. Listy*, 1956, **50** (10), 1593-1597.—The method described is suitable for use with biological materials. Fructose reacts, in conc. HCl soln., with indol-3-ylacetic acid to yield a blue-violet colour that can be used for analytical purposes. Conditions of the reaction and its specificity were studied. The determination can be carried out even in the presence of a large excess of aldoses; sorbose, tagatose and saccharides containing fructose interfere. *Procedure*—Mix the sample (1 ml) containing $<0.1\text{ mg}$ of fructose with the reagent (0.5% ethanolic soln.) (0.2 ml) and with conc. HCl (8 ml). Set aside overnight and measure the extinction at $530\text{ m}\mu$. Make a blank determination. The reaction may be carried out at 37° , and the extinction is then measured after 1 hr. The accuracy is within $\pm 2\%$. J. ŽYKA

1867. Polarography of unsaturated diketones of the type $R\cdot\text{CO}\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot R$. A. Ryvolová (Polarographic Inst., Acad. Sci., Prague, Czechoslovakia). *Chem. Listy*, 1956, **50** (12), 1918-1924.—The ethylenic bond of aliphatic compounds containing the conjugated system $\text{--CO}\cdot\text{CH}:\text{CH}\cdot\text{CO}\cdot\text{--}$, when polarographically reduced, yields, in buffered soln., one wave, the half-wave potential of which does not depend on the length of the aliphatic chain. When this chain is substituted by a benzene ring, the half-wave potential is shifted to more positive values. When irradiated, the *trans* form of the investigated compounds is converted to the *cis* form. By using polarographic and oscillographic methods, the differentiation of both isomers is possible. J. ŽYKA

1868. Spectrophotometric determination of traces of water in acetic acid. S. Bruckenstein (Univ. Minnesota, Minneapolis, U.S.A.). *Anal. Chem.*, 1956, **28** (12), 1920-1921.—The method involves addition of acetic anhydride to the acetic acid sample and spectrophotometric measurement of the unchanged anhydride after 90 min. heating at 110° . The analytical wavelength used was $252\text{ m}\mu$. Results were in good agreement with those obtained by the visual Karl Fischer procedure, and the method was also ten times as sensitive. G. P. COOK

1869. The separation of the C_6 to C_{12} fatty acids by reversed-phase partition chromatography. J. B. Wittenberg (Dept. of Biochem., Albert Einstein

Coll. of Med., Yeshiva Univ., New York, U.S.A.). *Biochem. J.*, 1957, **65** (1), 42-45.—Reversed-phase partition chromatography on columns of silicone-treated Hyflo Super Cel is used for the separation of the C_8 to C_{12} fatty acids. Two solvent systems are used—chloroform - Skellysolve S (a decane fraction) - water - methanol (8:15:12:20, by vol.) and the same components (8:1:75:11:20, by vol.). The method is also applicable to the separation of the terpene acids. J. N. ASHLEY

1870. Use of 2:4-dinitrophenylhydrazones of *p*-phenylphenacyl esters as second derivatives in identification of organic acids. Hawkins Ng, A. D. Webb and R. E. Kepner (Univ. of Calif., Davis, U.S.A.). *Anal. Chem.*, 1956, **28** (12), 1975-1977.—The 2:4-dinitrophenylhydrazones of the *p*-phenylphenacyl esters of 18 saturated fatty acids were prepared and their m.p. were determined. In several cases where the *p*-phenylphenacyl esters of acids have similar m.p., the phenylhydrazone derivatives prepared from them show considerable differences in m.p. In several instances, the identity of unknown acids can therefore be established by knowledge of the m.p. of the two derivatives. The double derivatives of the straight-chain saturated acids from acetic to octadecanoic can be separated on silicic acid - nitromethane chromatographic columns, and the R_F values obtained may be of assistance in the identification of a particular acid. G. P. Cook

1871. Analysis of acid chlorides containing free carboxylic acid and hydrogen chloride. C. R. Stahl and S. Siggia (Gen. Aniline and Film Corp., Easton, Pa., U.S.A.). *Anal. Chem.*, 1956, **28** (12), 1971-1973.—With the method described, the acid chloride as well as the free carboxylic acid and HCl in the sample can be determined. The free HCl in a chlorobenzene - ether soln. of the sample is titrated potentiometrically with tripropylamine. Another portion of the sample is titrated with NaOH after the acid chloride has reacted with added *m*-chloroaniline; two potential breaks are obtained, one due to the free carboxylic acid and the other due to the neutralisation of the free HCl and amine hydrochloride formed from the acid chloride. The acid chloride concn. is determined from the difference between the amine hydrochloride titration and the free HCl titration. Good results were obtained with various synthetic mixtures. G. P. Cook

1872. Compleximetry in organic analysis. IV. Semi-micro determination of nitro and nitroso compounds. B. Buděšínský (Res. Inst. Pharm. and Biochem., Prague, Czechoslovakia). *Chem. Listy*, 1956, **50** (12), 1931-1935.—The reduction of nitrobenzene and nitromethane with metallic Zn, Cd, Hg, Sn, Pb, Cu, Ni and zinc amalgam (2%) in HCl was studied. The results were used for the quant. determination of many nitro and nitroso compounds. In the reaction with metallic Cd, an equivalent amount of Cd^{2+} is produced, which can be determined compleximetrically. Procedure—Dissolve 0.8 mg-equiv. of the sample (the aromatic nitro group corresponds to 6 equiv., and the aromatic and aliphatic nitroso groups to 4 equiv.) in methanol (5 ml), add five flat discs of metallic Cd (diam. 8 mm, surface area 126 sq. mm) activated by shaking for 30 min. with 0.25 N HCl, and remove Cd in a stream of CO_2 . Add 0.7 M HCl (5 ml), close the flask and shake for 60 min. (120 shakes per min.). To the supernatant liquid in a titration flask add

buffer soln. (pH 10) (NH_4Cl - aq. NH_3) (5 ml) and Eriochrome black T as indicator, and titrate with 0.05 M EDTA (disodium salt). Make a blank determination. The presence of halogen causes high results in some cases. When determining picric acid and *p*-nitrophenol, Na_2SO_3 (0.5 g) must be added before making the soln. alkaline with the buffer soln. J. ŽYKA

1873. Determination of primary aliphatic amines by an acidimetric salicylaldehyde reaction. J. B. Johnston and G. L. Funk (Carbide and Carbon Chemicals Co., S. Charleston, W. Va., U.S.A.). *Anal. Chem.*, 1956, **28** (12), 1977-1979.—A measured excess of salicylaldehyde is treated with the primary amine in pyridine soln. and the excess of reagent is titrated with sodium methoxide to either phenolphthalein or thymolphthalein indicator. Aliphatic secondary and tertiary amines do not interfere, but ammonia and amine salts do. The accuracy is generally >96%. G. P. Cook

1874. A colorimetric method for the determination of aliphatic amines in the presence of ammonia. L. Ekladius and H. K. King (Dept. of Biochem., Univ. of Liverpool, England). *Biochem. J.*, 1957, **65** (1), 128-131.—A micro-method is described for the determination of lower aliphatic amines in biological material. The amine is steam-distilled at an alkaline pH and condensed with chloro-2:4-dinitrobenzene. The resulting yellow product is then determined spectrophotometrically at 450 mμ. Ammonia does not interfere in the method, which might be suitable for the determination of some secondary amines. The accuracy of the method is within $\pm 2\%$. J. N. ASHLEY

1875. Determination of volatile aliphatic amines in the presence of ammonia in non-volatile preparations. Z. Bellen (Anal. Dept., Chem. Inst., Warsaw). *Chem. Anal., Warsaw*, 1956, **1** (1), 71-75.—The procedure is based on that developed by Weber and Wilson (*J. Biol. Chem.*, 1918, **35**, 385), in which yellow mercuric oxide is used for absorbing ammonia. In the present method the filtration is carried out under enclosed conditions and this makes it possible to attain an accuracy of $\pm 1\%$ on amounts up to 1.5%, calculated as dimethylamine. The amines and ammonia are distilled in the usual way from an alkaline soln. into a 500-ml bottle and the distillate is treated with alkali and yellow mercuric oxide. The mixture is shaken for 1 hr. and set aside overnight. The bottle is then closed with a rubber stopper carrying a short glass inlet-tube and a tube that dips into the test mixture and is connected to a stoppered sintered-glass filter funnel, whose stem passes through a rubber bung into a flask containing dil. HCl. By evacuating the flask, the soln. from the bottle is sucked into the filter funnel, and then into the flask with no possibility of losing vapours of volatile amines. The method was found to be satisfactory for the determination of volatile aliphatic amines in hexamine. K. F. SPOREK

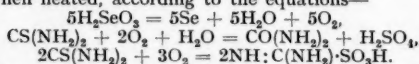
1876. The analysis of preparations based on ethylenediaminetetra-acetic acid. H. Abdine (School of Pharmacy, Univ. Alexandria, Egypt). *Arzneimittel-Forsch.*, 1956, **6** (12), 698-700.—Rapid and accurate methods are described for the determination of both EDTA (I) and a metal (II) in complexes of I with II. For complexes of I with Ca, Mg or Mn, I is determined by adding 0.01 M $CuSO_4$ with constant shaking to a soln. of the sample in

dil. acetic acid until the indicator [1-(2-pyridylazo)-2-naphthol] turns violet and back-titrating with 0.01 M EDTA (disodium salt) (III) at the b.p. to a yellow end-point. To determine II, the titration with III is continued after bringing the pH to 10 with aq. NH_3 - NH_4Cl buffer. For complexes of I with Fe, Co or Cu, the procedure depends on whether I or II is present in excess. Excess of II is determined by direct titration with III in boiling soln.; excess of I is determined by addition of 0.01 M CuSO_4 and back-titration with III, as above. The total amount of I is determined by adjusting the pH of a fresh sample to 10, adding KCN and (if II is Fe) ascorbic acid, heating to boiling, cooling to 50°, adding 0.01 M MgSO_4 until the indicator (Eriochrome black T) turns red, and back-titrating with III to a blue end-point. A. R. ROGERS

1877. The identification of mercaptans with 2:4-dinitrobenzenesulphenyl chloride. H. Böhme and H. Stachel (Inst. für Pharm. Chemie und Lebensmittelchemie, Univ. Marburg, Lahn, Germany). *Z. anal. Chem.*, 1957, **154** (1), 27-28.—Aliphatic and aromatic mercaptans form crystalline disulphide derivatives with 2:4-dinitrobenzenesulphenyl chloride. A table of melting-points of several such derivatives is given. M. F. C. LADD

1878. Paper chromatography of the primary condensation products of formaldehyde and thiourea. K. Dušek (Res. Inst. Synth. Resins, Pardubice, Czechoslovakia). *Chem. Listy*, 1956, **50** (12), 1948-1953.—For the separation of homologous poly(methylene thioureas) and methoxymethyl deriv. of thiourea, a mixture of ethyl methyl ketone and butyl methyl ketone (5:1) saturated with H_2O was used. For the separation of hydroxymethyl deriv., a mixture of methanol and H_2O (7:1) as solvent and a paper impregnated with buffer soln. (pH 6.9) was suitable. For detecting hydroxymethyl deriv., a soln. of phenylhydrazine (1.8% soln. in isopropyl alcohol), $\text{K}_2\text{Fe}(\text{CN})_6$ (25% aq. soln.) and 2 M NaOH has been found to be a specific reagent. R_F values of ten compounds are given. J. ŽYKA

1879. Selenous acid, a quantitative oxidant for thiourea. M. K. Joshi (Anal. Lab., Hindu Univ., Benares, India). *Chem. Listy*, 1956, **50** (12), 1928-1930.—Selenous acid quant. oxidises thiourea when heated, according to the equations—



The excess of selenous acid can be determined iodimetrically, or the reduced selenium gravimetrically. *Procedure*—Heat 10 to 20 ml of 0.1 N H_2SeO_3 on the water bath (50° to 60°) in 3 to 5 N HCl, add 5 to 10 mg of thiourea, heat under reflux (15 to 30 min.), cool and filter. Either wash the pptd. Se with warm H_2O , ethanol and ether, dry at 120° to 130° and weigh; or dilute the filtrate to 500 ml and determine the excess of H_2SeO_3 iodimetrically in an aliquot. J. ŽYKA

1880. Colorimetric estimation of dialkyl phosphites in presence of trialkyl phosphites, phosphates and phosphonates. S. Sass and J. Cassidy (Army Chemical Center, Md., U.S.A.). *Anal. Chem.*, 1956, **28** (12), 1968-1970.—The method is based on the reaction of dialkyl hydrogen phosphites with 1:3:5-trinitrobenzene to form a red colour with an absorption max. at 465 m μ . The colour reaction is specific for the dialkyl phosphites in the presence

of other phosphites, phosphates or phosphonates. Beer's law is obeyed over the concn. range 5 to 30 μg per ml; recoveries are $\approx 100\%$; and the sensitivity is 0.2 to 0.5 μg per ml. G. P. COOK

1881. Chromatothermographic method of determining benzene, toluene, isopentane, hexane and isooctane. L. S. Chemodanov and N. M. Turkel'taub (Inst. of the Hygiene of Work and Professional Diseases, Acad. Med. Sci., U.S.S.R.). *Zavod. Lab.*, 1956, **22** (12), 1406-1407.—The hydrocarbons are adsorbed on silica gel, air at a rate of 115 ml per min. is used for developing the chromatogram, and a temp. of 160° is used for quant. desorption and separation of benzene, toluene, isopentane, hexane and isooctane. The method is sensitive to 0.8 mg of benzene per litre and 1 mg of toluene per litre, and the accuracy is within $\pm 7\%$. G. S. SMITH

1882. Chromatographic method of separate determination of divinyl, ethylbenzene and styrene in air. F. D. Krivoruchko and N. M. Turkel'taub (Inst. of the Hygiene of Work and Professional Diseases, Acad. Med. Sci., U.S.S.R.). *Zavod. Lab.*, 1956, **22** (12), 1408-1409.—Divinyl is completely desorbed from silica gel by means of air at 70° to 85°, ethylbenzene is desorbed at 170°, but styrene, which is polymerised at these temp., becomes depolymerised and capable of desorption only at 300°. The separate components can be determined in a mixture with an error of $\pm 9\%$. G. S. SMITH

1883. Quantitative determination of phenol and o-cresol by paper chromatography. S. Hudeček and D. Beranová (Res. Inst. Synth. Resins, Pardubice, Czechoslovakia). *Chem. Listy*, 1956, **50** (9), 1456-1458.—The quant. determination of phenols and o-cresol in various types of phenolic resin has been developed; the average error is $\pm 5\%$. To prevent volatilisation, the determinations were carried out between two glass sheets. The chromatograms were eluted with a mixture of cyclohexanone, chloroform and ethanol (21:9:0.6) and the phenolic group was detected with a soln. of diazotised p-nitroaniline. The quantitative evaluation was made by planimetry. The method yields good results in comparison with the usual bromimetric determination. J. ŽYKA

1884. A colour reaction of flavanonols. H. Pacheco and M. Chadenson. *Compt. Rend.*, 1956, **242** (12), 1621-1624.—Flavanonols, acetylated in boiling acetic anhydride, with anhyd. Na acetate, give bright-red compounds. These, treated with HCl, are converted into red pigments with the characteristics of flavylium chlorides. This reaction is specific to flavanonols, and none of the related substances behaves in the same way. Their spectrum shows a band between 510 and 545 m μ , and, by paper chromatography, each of the substances shows a single stain. The pigments appear to be identical with those derived from hydroxyflavones treated with acetic anhydride and zinc. J. F. P. H. GREENE

1885. The estimation of dinitrophenyl compounds by quantitative hydrogenation in a Warburg apparatus. H. Hörmann, J. Lamberts and G. Fries (Max Planck Inst., Regensburg, Germany). *Hoppe-Seyl. Z.*, 1956, **306** (1), 42-48.—The method described is based on the reduction of the nitro groups with H and measurement of the H absorbed. *Procedure*—A known quantity of the test substance

(0.1 to 0.6 mg) is dissolved in 0.1 to 0.4 ml of a suitable solvent (100% ethanol or pyrrolidine) and hydrogenated in the presence of 1 ml of the pure solvent mixed with 2 mg of the catalyst (5% of PdO in BaSO₄); an accuracy of $\pm 4\%$ is attained. The method is also useful for the determination of dinitrophenylated amino groups, as well as for other phenolic hydroxyl groups which are readily substituted by the dinitrophenyl group. Comparisons are made with the standard colorimetric method.

G. R. WHALLEY

1886. Paper chromatography of nitrotoluidines.

I. Separation and identification of isomeric mononitro derivatives of o-toluidine. A. Waksmundzki, J. Ościk and Z. Frelek (Lublin Univ., Poland). *Ann. Univ. M. Curie-Skłodowska, [A]*, 1954, [1956], 9, 83-89.—Satisfactory separation was achieved by ascending chromatography on paper of moisture content 33%, with water-saturated n-hexane as the ascending phase. The R_F values obtained were 0.90, 0.59, 0.46 and 0.16, respectively, for the 3-, 6-, 4- and 5-nitro-o-toluidines; these values are related to the dipole moments of the respective isomers.

R. TRUSCOE

1887. Fluorimetric titration of the 2-naphthylaminomonosulphonic acids. F. Čůta and J. Boreký (Inst. Anal. Chem., Vysoká škola chemická, Prague, Czechoslovakia). *Chem. Listy*, 1956, 50 (9), 1432-1438.—Two procedures for the determination of individual 2-naphthylaminomonosulphonic acids, based on the dependence of the total intensity of fluorescence on the concentration of the acid at a constant pH, as well as the decrease of fluorescence of one of the acids by the addition of aluminium nitrate, were developed. With both these methods, a calibration curve must be constructed (error ± 1.6 and $\pm 2.8\%$). Approximate results (error $\pm 15\%$) can be obtained without a calibration curve, if a linear relation is assumed to exist between the concn. of corresponding acid and the difference of the fluorescence intensity. By using a nomogram, a mixture of three 2-naphthylaminomonosulphonic acids can be analysed. The most suitable concn. of sample is 10^{-3} M.

J. ZYKA

1888. Determination of naphthalene-2:6-disulphonic and naphthalene-2:7-disulphonic acids in the presence of each other. W. Czerwiński (Anal. Dept., Chem. Inst., Warsaw). *Chem. Anal., Warsaw*, 1956, 1 (1), 77-83.—The method is based on the different solubilities of the benzidine salts of the two acids. Owing to the slight solubility of the 2:7-acid salt under the conditions used, a correction factor has to be applied. *Procedure*—Dissolve 1 to 2 g of the acids in 50 to 100 ml of water, neutralise exactly with 0.5 N NaOH and dilute with water to 175 ml. Heat to boiling-point, add 25 ml of 10% BaCl₂ soln., followed by 50 ml of benzidine hydrochloride soln. [dissolve 20 g of benzidine in 200 ml of water, add 25 ml of conc. HCl (sp. gr. 1.19), mix, cool, and dilute with water to 1 litre], then heat again to boiling-point. Allow to cool to a temp. of 62° to 65°, and filter rapidly through a sintered-glass crucible provided with a heating jacket kept at 66°. Wash the ppt. with a little water (at 63°), then transfer it quantitatively to the original beaker, add 50 ml of the benzidine hydrochloride soln. and cool to between 62° and 65°. Filter as above and wash the ppt. with hot water until it is free from chloride. Dissolve the ppt. in 50 ml of 95% ethanol and titrate with 0.1 N NaOH. Calculate the 2:6-acid content as follows.

$x (\%) = (14.4 \times a_1)/G$, where a_1 is vol. (ml) of 0.1 N NaOH and G is the wt. (in grams) of sample taken. Weigh an identical quantity of the sample as above, separate the 2:6-acid, then precipitate the 2:7-acid from the filtrate by cooling to 0°. Wash the ppt. with water cooled to nearly 0°, and finish the determination in exactly the same way as for the 2:6-acid. Calculate the 2:7-acid content as follows— $y (\%) = (14.4 \times a_2 + 2.26)/G$, where a_2 is vol. (ml) of 0.1 N NaOH, 2.26 is the correction for solubility and G is the wt. (in grams) of sample taken.

K. F. SPOREK

1889. Detection and determination of thujone by paper chromatography, a contribution to the analysis of aldehydes and ketones of the terpene series. P. H. Joppien (Chem. und Lebensmitteluntersuchungsanstalt im Hyg. Inst., Hamburg). *Z. Lebensmittelforsch.*, 1956, 104 (6), 393-401.—Thujone is separated as its 2:4-dinitrophenylhydrazone by paper chromatography and determined spectrophotometrically at 360 m μ ; as little as 5 μ g can be determined. The use of this method for the determination of other terpene carbonyl compounds in essential oils, in drugs and in muscatel and vermouth wines is discussed. S.C.I. ABSTR.

1890. Review of analytical methods for the determination of trace quantities of hydrocarbons. J. J. Glogoczowski (The Geo-anal. Dept., Petroleum Inst., Krakow). *Chem. Anal., Warsaw*, 1956, 1 (1), 5-19.—An extensive survey is presented of the problems encountered in oil prospecting and the various methods used for the determination of hydrocarbons in rocks, water and air at concn. of 10^{-2} to 10^{-4} % by vol. A mass spectrometer is considered the most efficient and promising tool for the purpose, with the added advantage that very small quantities of the sample (0.1 to 0.0001 ml) are required for a complete determination of components. This makes it possible to determine hydrocarbons adsorbed on to grains of rock or dissolved in water. With a sample of gas of 0.00138 ml, 12 components were determined with errors ranging from 0.1 to 3.6%. Literature references (21) for the period 1941-1954 are quoted.

K. F. SPOREK

1891. Fluorescent indicator adsorption method for hydrocarbon-type analysis. Application to traces and heavier distillates. H. S. Knight and S. Groennings (Shell Development Co., Emeryville, Calif., U.S.A.). *Anal. Chem.*, 1956, 28 (12), 1949-1954.—The method of Conrad (*Anal. Chem.*, 1948, 20, 725), in which the aromatic portion of petrol in a chromatographic column is rendered visible in u.v. light by addition of a fluorescent indicator, has been extended to the determination of hydrocarbon types in smaller than normal concn. and to the analysis of cracked gas oils and lubricating oils. The composition of the oil is computed from the lengths of the visible zones. When applied to lighter petroleum distillates, the accuracy is within $\pm 0.05\%$ for concn. below 0.5% and within $\pm 0.10\%$ for higher concn. The accuracy is about the same for the determination of traces of saturates and olefins in aromatics and for a trace of olefin in a saturate-aromatic mixture. The reliability of the method for heavier distillates is within $\pm 2\%$.

G. P. COOK

1892. Hydrocarbons in the 126° to 132° C fraction of petroleum. M. B. Epstein, C. B. Willingham, B. J. Mair and F. D. Rossini (Carnegie Inst. Technol., Pittsburgh, Pa., U.S.A.). *Anal. Chem.*,

1956, **28** (12), 1924-1927.—Seven hydrocarbons were found in the petroleum fraction boiling between 126° and 132°. The compounds were concentrated by distillation and adsorption techniques and were identified by i.r. and mass spectrometry, coupled with measurements of the simple physical properties. The compounds found were—ethylcyclohexane (53%); 1-*trans*-2-*cis*-3-*trans*-4-tetramethylcyclopentane (16%); 1-*cis*-2-dimethylcyclohexane (9%); *n*-propylcyclopentane (9%); 1-methyl-*cis*-2-ethylcyclopentane (6%); 2:3:5-trimethylhexane (5%); and isopropylcyclopentane (2%). G. P. COOK

1893. Determination of saturated hydrocarbons in heavy petroleum fractions by mass spectrometry. H. E. Lumpkin (Humble Oil and Refining Co., Baytown, Tex., U.S.A.). *Anal. Chem.*, 1956, **28** (12), 1946-1948.—A mass-spectrometric method is described for determining paraffins, non-condensed naphthenes and condensed naphthenes containing two to six condensed rings per molecule. The characteristic mass groupings for each type of compound were determined and are listed. Sensitivity and interference coefficients were determined from the averages of pure compound spectra and extrapolated data. The method is simple and rapid, lending itself to inverted matrix and computer calculation. G. P. COOK

1894. Relationship between carbon-type composition, viscosity-gravity constant, and refractivity intercept of viscous fractions of petroleum. S. S. Kurtz, jun., R. W. King, W. J. Stout, D. G. Partikian and E. A. Skrabek (Sun Oil Co., Marcus Hook and Norwood, Pa., U.S.A.). *Anal. Chem.*, 1956, **28** (12), 1928-1935.—A triangular graph is described which relates carbon-type composition in terms of percentage aromatic, naphthenic and paraffinic carbons to viscosity-gravity constant and refractivity intercept for viscous petroleum fractions. Viscosity, gravity and refractive-index measurements enable carbon-type composition to be determined fairly accurately; oils having a viscosity-gravity constant of 0.900 or less give standard deviations for the three types of $\approx 1.5\%$, and for constants between 0.900 and 1.00 the standard deviations are $< \pm 5\%$; samples containing $< 30\%$ of C in aromatic rings give standard deviations of between ± 1.0 and 2.0% . G. P. COOK

1895. Differential infra-red spectrometry; its application to analysis in the petroleum industry. H. Powell (British Petroleum Co., Sunbury-on-Thames, England). *J. Appl. Chem.*, 1956, **6** (11), 488-494.—By means of the technique described, the absorption of one or more components of a mixture can be completely eliminated from the recorded spectrum without serious loss of detail in the residual spectrum. Applications to the qual. and quant. analyses of petroleum products and to insecticides containing kerosene are given. K. A. PROCTOR

1896. Composition of lubricating oil. Use of newer separation and spectroscopic methods. F. W. Melpolder, R. A. Brown, T. A. Washall, W. Doherty and C. E. Headington (Atlantic Refining Co., Philadelphia, Pa., U.S.A.). *Anal. Chem.*, 1956, **28** (12), 1936-1945.—A study of the composition and physical properties of fractions separated from a heart cut of a solvent-refined oil is presented. The oil charge was separated by means of 20-stage molecular distillation, silica gel chromatography and liquid thermal diffusion to yield 43 fractions containing concentrates of paraffins and cyclo-

paraffin hydrocarbons. Refractive indices and pycnometer densities were measured for each fraction, hydrocarbon-type analyses were determined by high-temp. mass-spectrometry, and supplementary information on molecular structure was obtained from u.v. and i.r. spectrometry. The accuracy of the mass-spectrometric method was determined by measuring synthetic blends, and values for the major constituents—paraffins, mono-, di- and tri-cycloparaffins—generally agreed with the known values to within $\pm 10\%$ relative. Smaller components differed by 0.2 to 2.3% absolute. Infra-red and u.v. analyses were used to confirm the mass-spectrometric data. G. P. COOK

1897. Determination of nitrogen in solid fuels by a modified macro-Dumas method. N. G. Banerjee and N. C. Saha (Fuel Res. Inst., Jealgarh, Bihar). *J. Inst. Chem. India*, 1956, **28** (3), 271-280.—By the use of the modifications described, reproducible results are obtained. I. JONES

1898. Factors affecting use of dielectric methods in determination of sea water in Navy Special fuel oil. T. D. Callinan, R. M. Roe and J. B. Romans (U.S. Naval Res. Lab., Washington, D.C., U.S.A.). *Anal. Chem.*, 1956, **28** (12), 1911-1916.—Measured values of the dielectric const. (ϵ), power factor (%), dielectric-loss factor, and electrical conductivity of 19 fuel oils show considerable variation at comparable frequencies from 10 kc to 75 Mc. When these oils are emulsified with synthetic sea water, the observed values increase with increasing content (S) of sea water, but remain a function of the properties of the original dry oil. The values of ϵ for the oil are dependent on frequency, indicating the presence of varying amounts of polar compounds. Over the range $\epsilon = 2.5$ to 5, measured at 1 or 75 Mc, the calculated values of S (up to 25%) can be in error by 3 to 7%. Other variables may cause more serious errors. When the error is likely to exceed $\pm 20\%$, the determination of S in fuel oil by measurement of ϵ is impracticable. The necessity for using a dry reference sample is emphasized. W. J. BAKER

1899. Chromatography of dyestuffs intermediates. V. Naphthylamine- and naphthol-sulphonic acids. J. Latínák and L. Skalický (Východočeské chemické závody, Pardubice-Rybitví, Czechoslovakia). *Chem. Listy*, 1956, **50** (10), 1598-1601.—Naphthylamine- and naphthol-sulphonic acids were separated chromatographically by using the system *n*-propanol-aq. NaHCO₃ soln. (2:1). The use of chromatographic paper impregnated with NaHCO₃, and the characteristic changes of the position of the spots of the compound were studied, and possibilities of analysing dyestuffs intermediates are described. The R_F values of 20 naphthylamine- and 15 naphthol-sulphonic acids, obtained by the use of impregnated and unimpregnated paper, are presented. The procedure was analogous with that described previously (cf. Latínák, *Anal. Abstr.*, 1955, 2, 2141, 3102). J. ZÝKA

1900. Determination of the active dye in commercial litmus. N. Bellen and Z. Bellen (Anal. Dept., Chem. Inst., Warsaw). *Chem. Anal., Warsaw*, 1956, **1** (1), 65-69.—Purified azolitmin, prepared from ordinary litmus by the method described, was used to establish the optimum conditions and the coefficient of absorption in the colorimetric determination of the substance in crude litmus. Procedure—Weigh into a 100-ml standard flask enough

of the finely ground sample to provide 0.01 to 0.05 g of azolitmin, add 10 ml of water and mix. Add 49.9 ml of 0.1 N NaOH and make up to volume with 0.2 M sodium tetraborate. Allow to stand for 5 min. and filter. Reject the first 20 ml of the filtrate, and measure the extinction of the remainder at 600 m μ . K. F. SPOREK

1901. The detection of micro quantities of gelatin. P. Davis (Kodak Ltd., Wealdstone, Middlesex, England). *J. Appl. Chem.*, 1956, **6** (10), 413-415.—Gelatin can be detected by the method described at a concn. as low as 4×10^{-8} g per ml, in the presence of large quantities of electrolyte. The method, which can be made semi-quant., involves concn. of the soln. by foaming, and detection of the gelatin by means of a modified Zsigmondy gold sol test. K. A. PROCTOR

1902. Colorimetric determination of reducible sulphur in pulp and paper. I. Sobolev, R. Bhargava, N. Geacintov and R. Russell. *TAPPI*, 1956, **39** (9), 628-638.—Part of the total S in the sample is reduced to H₂S, and then treated with *p*-aminodimethylaniline to form methylene blue. The percentage of total S in the sample, determined as reducible S, is greater than that obtained by TAPPI standard T 406 m-53. With a 0.5-g sample, results are reproducible within ± 1 p.p.m. of reducible S; with a 2-g sample, concn. as low as 0.5 p.p.m. can be detected. The determination takes less than 2 hr. S. V. SERGEANT

1903. Measurement of odour. D. R. Duncan (Paint Research Station, Teddington, England). *Paint Tech.*, 1956, **20**, 243.—A short account is given of the progress that has been made towards the measurement of odour, including the use of the air-dilution olfactometer for the assessment of odour intensity and of selective odour fatigue in the classification of odours. D. R. DUNCAN

1904. Note on the separation of aldehydes and ketones [from orange oil] by means of Girard P reagent. A. Weissenberg and D. Ginsberg (Technion—Israel Inst. of Technol., Haifa). *Bull. Res. Council Israel*, A, 1956, **5**, 268-269.—Carbonyl compounds were isolated from Israel orange oil by means of Girard P reagent under the conditions given by Girard and Sandulesco (*Helv. Chim. Acta*, 1936, **19**, 1905). The substituted hydrazones were decomposed to carbonyl compounds, converted into 2:4-dinitrophenylhydrazones and separated by chromatography. In addition to those of carvone and pulegone, the 2:4-dinitrophenylhydrazone of *n*-decaldehyde was obtained, although Girard and Sandulesco state that the acetylhydrazones of aldehydes do not decompose under the conditions employed. The derivative obtained by treating synthetic *n*-decaldehyde in the same manner proved to be identical. G. BURGER

1905. Use of fluorescent indicators for the determination of small amounts of surface-active compounds. I. Determination of organic sulphates and sulphonates. M. Doležil (Výzk. ústav zůslecht. rud, Prague, Czechoslovakia). *Chem. Listy*, 1956, **50** (10), 1588-1592.—In the titrimetric method described, a quaternary salt of the cetyltrimethylammonium bromide type is used as volumetric reagent, with a fluorescent indicator. *Procedure*—Dissolve the sample (0.25 g) in a small vol. of warm water and dilute to 250 ml with twice-distilled water. To an aliquot add a soln. of eosin (0.2%) (0.05 ml),

neutralise if necessary, and titrate, while stirring, with a soln. of cetyltrimethylammonium bromide, in u.v. light, till the colour changes to red-violet. Make a blank determination. The error was $\pm 5\%$. J. ZÝKA

1906. Detection of surface-active alkylarylsulphonates by alkaline fusion and formation of an azo dye. M. J. Rosen and G. C. Goldfinger (Brooklyn Coll., Brooklyn, N.Y., U.S.A.). *Anal. Chem.*, 1956, **28** (12), 1979-1981.—The arylsulphonate is first fused with molten KOH and the phenol produced is detected by reaction with diazotised dianisidine; the dye colour may be purple, red or orange. Data for 34 commercial surfactants are listed. G. P. COOK

1907. Formaldehyde condensations with phenol and its homologues. XVIII. Chromatographic analysis. S. R. Finn and J. W. James (Vulcan Products Ltd., Argyll Avenue, Slough, England). *J. Appl. Chem.*, 1956, **6** (10), 466-476.—Phenol-formaldehyde reaction mixtures can be studied over a wide range of conditions by means of various chromatographic and experimental techniques. From the results obtained, a tentative hypothesis has been formed regarding the reaction mechanism involved in these condensations. K. A. PROCTOR

1908. Critical evaluation of some procedures for the analysis of urea-formaldehyde resins. J. Seidl and M. Vařta (Res. Inst. Synth. Resins, Pardubice, Czechoslovakia). *Chem. Listy*, 1956, **50** (12), 2031-2034.—When determining hydroxymethyl groups in urea-formaldehyde resins by means of commonly used methods, the presence of ethers and similar deriv. of these compounds in technical products causes interference. The stability of these functional groups was studied by the use of alkaline and acid hydrolysis. The Jong method (*Rec. Trav. Chim. Pays-Bas*, 1952, **71**, 643) was found suitable for this purpose. Formaldehyde liberated in alkaline medium reacts with KCN and the excess of cyanide is determined by titration with Hg(NO₃)₂, with diphenylcarbazone as indicator. When determining the stability in acid medium, the sample is treated with phenol in the presence of toluene-*p*-sulphonic acid and the liberated water is determined by means of the Karl Fischer titration. *sym*.-Di(hydroxymethyl)urea, di(phenylureido-methyl) ether, methylphenylbisphenylurea and *sym*.-di(methoxymethyl)urea were used for studying this method. J. ZÝKA

1909. Determination of methyl methacrylate by means of the ultra-violet absorption spectrum of the vapour. A. N. Shabadash and L. A. Igonin (State Sci. Res. and Planning Inst. of the Plastics Industry). *Zavod. Lab.*, 1956, **22** (11), 1324-1327.—The volatile material to be analysed is placed in an ampoule which is inserted in a special cell. The cell is evacuated, the ampoule is broken, and the absorption spectrum of the vapour is registered. The method is applied to the determination of the monomer in poly(methyl methacrylate) at 245 m μ . Soln. in dichloroethane are used. By means of a calibration graph the monomer can be determined within $\pm 0.05\%$ of the sample wt. G. S. SMITH

1910. Direct titration of oxirane oxygen with hydrogen bromide in acetic acid. A. J. Durbetaki (Food Machinery and Chem. Corp., Station B, Buffalo, N.Y., U.S.A.). *Anal. Chem.*, 1956, **28** (12), 2000-2001.—The sample is directly titrated

with standard HBr in acetic acid soln. to the endpoint with crystal violet indicator. Epoxy resins are first dissolved in CHCl_3 and other compounds in chlorobenzene or benzene. The method is applicable to a variety of epoxy compounds, epoxy resins and epoxy plasticisers. Carboxylic acids, aldehydes, ethers, esters and peroxides do not interfere. The reproducibility and accuracy are generally within $\pm 0.4\%$. G. P. COOK

1911. Determination of borax in borax-cut shellac. W. K. Miller, O. Tweet, R. H. Simon and D. E. Whyte (S. C. Johnson & Son, Inc., Racine, Wis., U.S.A.). *Soap*, N.Y., 1956, **32** (11), 147, 157.—A 5-g sample of the shellac is weighed into a separating funnel (125 ml) and 50 ml of butanol and 50 ml of water are added. Conc. HCl is added dropwise to give a permanent red colour with methyl red indicator, and two drops of HCl are added in excess. The mixture is shaken, allowed to stand, and the aq. layer drained into a titration flask (250 ml). The extraction is repeated with water (2×50 ml). A few drops of methyl red indicator are added to the combined aq. extracts and 0.1 N NaOH is added until the red colour is just discharged. One drop of 0.1 N HCl is added to restore the colour, followed by 2 g of mannitol and 1 ml of aq. phenolphthalein, and the solution is titrated with 0.1 N NaOH. S.C.I. ABSTR.

See also Abstracts 1737, 1740, 1809, 1935, 1936, 1937, 1982, 1996, 1999.

4.—BIOCHEMISTRY INCLUDING DRUGS, FOOD, SANITATION, AGRICULTURE

Blood, Bile, Urine, etc.

1912. Blood pH measurement with the glass electrode. S. Natelson and N. Tietz (Rockford Memorial Hosp., Rockford, Ill., U.S.A.). *Clin. Chem.*, 1956, **2** (5), 320-327.—The tendency of blood obtained by finger-prick from normal individuals to drift to alkaline pH values more rapidly than venous blood is ascribed to a release of carbonic anhydrase into the serum in greater quantity when the finger is punctured than occurs with venepuncture. In determining blood pH, the specimen should be collected under oil, the serum rapidly separated, and the determination performed on the separated serum under oil.

H. F. W. KIRKPATRICK

1913. Utilisation of spectrography for the simultaneous determination of cations in solution. [With application to plasma and whole blood.] R.-Y. Mauvernay. *Compt. Rend.*, 1956, **242** (10), 1316-1318.—The method may be used for biological or other solutions. Chemical pre-treatment is necessary for biological solutions, to destroy the organic matter, so as to avoid irregular vaporisation at the excitation source. It is carried out by heating the solution with an acid containing a metal to act as reference; after being dried, the product is dissolved in water. The lower electrode used in the process is a graphite disc, driven at 5 r.p.m. An arc initiated by a spark is used, the spark being at about 12,000 V; its isochronism is regulated to $\pm 10^{-4}$ sec. The arc pulses, of about 10^{-2} sec., are of the order of 10 amp. The plates employed are sensitive from 220 to 500 $\mu\mu$. In 1 ml of solution containing 30 μg each of Mn, Cu, Co, Zn and Fe, the greatest

error recorded is 2.4%. This determination has been repeated at monthly intervals with precisely reproduced results. A total of 7400 successful tests has been made on biological liquids, and 2000 on complex solutions. The accuracy has been equal to or better than that attainable by the other methods applicable. J. F. P. H. GREENE

1914. Estimation of mercury in urine and blood. E. Hintzsche. *Chem. Tech., Berlin*, 1956, **8** (11), 670-672.—A new, accurate and more rapid method comprises (i) chlorinating and evaporating the sample to dryness, (ii) treating the residue with hot conc. H_2SO_4 in the presence of NaCl and collecting the vapour containing the "liberated" Hg in water, and (iii) estimating the Hg in the resulting strongly acid solution by extractive titration with dithizone in CCl_4 (cf. Fischer and Leopoldi, *Z. anal. Chem.*, 1935, **103**, 441). *Procedure for urine*—The sample (1 litre) is acidified to a pH of 2 to 3 with conc. HCl if not already acid to Congo red paper; a rapid stream of Cl_2 is passed through, first at room temp. for 5 min. (to ensure solution of all Hg), and then at 90° to 95° till the sample is colourless. The solution is filtered from pptd. albumin and to <100 ml of filtrate is added 3 g of NaCl and the mixture is evaporated at 75° on the water bath (overnight). The damp residue is transferred to a quartz flask (with dropping funnel) connected, via a quartz-packed quartz tube heated to $\approx 800^\circ$, to a water-filled receiver and a vacuum pump. Conc. H_2SO_4 (30 ml) is added dropwise to the flask and after the reaction subsides the mixture is boiled; 20 to 30 drops of saturated NaCl solution are added dropwise and the mixture is again brought to boiling-point. To the contents of the receiver (or an aliquot if the content of Hg is $>1000 \mu\text{g}$ per litre) ≈ 1 g of urea is added and the mixture is transferred to a 500-ml separating funnel. A standard solution of dithizone in CCl_4 is added in measured small amounts with shaking (≈ 30 sec.) until the green colour persists or is discharged (depending on the pH). *Procedure for blood*—A 20-ml sample is coagulated in a test-tube, then dissolved by the gradual addition of 10% aq. Na acetate; ≈ 25 ml of chlorine water is added to ensure solution of all Hg from the walls of the tube. Chlorination and the later stages of the determination are carried out as described above. Test analyses prove the accuracy of the method. Other metals used in medicine and likely to be found in urine appear to have but slight effect on the titration; the actual effects of large dosages of Cu, Sb, As and Bi are demonstrated by test analyses. H. L. WHITEHEAD

1915. Vanadium concentration in urine. Rapid colorimetric method for its estimation. W. T. Rockhold and N. A. Talvitie (Eaton Lab., Div. of Norwich Pharmacal Co., Norwich, N.Y., U.S.A.). *Clin. Chem.*, 1956, **2** (3), 188-194.—A rapid semi-quantitative screening test for absorption of V is as follows. To 1 ml of test urine and to 1 ml of control urine of an individual having no exposure to V add 1 ml of saturated KClO_3 soln. and 1 ml of colour reagent (1% soln. of *p*-aminodiethylaniline monohydrochloride in glacial acetic acid), mix and place in a boiling-water bath. After heating the tubes for 15 min. cool them quickly and read the colours at 540 $\mu\mu$. Standards containing up to 1.0 μg of V are prepared by adding aliquots of a soln. containing 100 μg of V per ml (0.2296 g of ammonium metavanadate dissolved in 25 ml of 4 N H_2SO_4 and diluted to 1 litre with water) to V-free urine and developing similarly. The test is

sensitive to 0.01 μg of V per ml of urine, but the colour becomes too intense to differentiate above 1 μg per ml.
H. F. W. KIRKPATRICK

1916. Serum iron determination. G. R. Kingsley and G. Getchell (Dept. of Physiol. Chem., School of Med., Univ. of California, Los Angeles, U.S.A.). *Clin. Chem.*, 1956, **2** (3), 175-183.—Pipette 1 ml of fresh unhaemolysed serum and 1 ml of water for the blank into glass-stoppered tubes (16 mm \times 150 mm). Add 3 ml of water and 2 ml of N HCl and heat in boiling water for 30 min.; cool, add 2 ml of saturated aq. Na acetate, 6 ml of iron reagent and 0.5 ml of saturated aq. hydrazine sulphate. Stopper the tubes, shake in a Kahn shaker for 15 min., remove the stoppers and centrifuge. Pipette off 5 ml of the isoamyl alcohol layer, clear by adding 0.5 ml of absolute ethanol and read the test against the blank at 530 m μ . Standardise by treating aliquots of up to 4 ml of standard iron soln. (1 ml \equiv 1 μg of Fe) as described above and construct a graph. The iron reagent used is 70 mg of 4:7-diphenyl-1:10-phenanthroline dissolved in isoamyl alcohol and diluted with the solvent to 500 ml. The normal range by this method is 120 to 200 μg of Fe per 100 ml of serum for women, and 125 to 238 μg of Fe per 100 ml of serum for men.
H. F. W. KIRKPATRICK

1917. Determination of thorium in urine. R. W. Perkins and D. R. Kalkwarf (Gen. Electric Co., Richland, Wash., U.S.A.). *Anal. Chem.*, 1956, **28** (12), 1989-1993.—Concn. of Th in urine as low as 0.05 μg can be determined spectrophotometrically as the Th-morin complex. In the procedure described, the sample (500 ml) is evaporated to \approx 30 ml with 100 ml of conc. HNO_3 and 2 ml of $\text{La}(\text{NO}_3)_3$ soln. (\approx 20 mg of La). The cooled soln. is centrifuged and Th is removed from the filtrate by co-pptn. with LaF_3 ; two pptn., each with 5 ml of conc. HF, are made, centrifuging each time. The ppt. is digested with 2 N HNO_3 (10 to 15 ml) and conc. HClO_4 (3 ml), and the soln. is evaporated to dryness. The residue is dissolved in 3 ml of N HNO_3 and the Th is then separated from remaining urine salts and the lanthanum carrier by extraction with 10 ml of 0.45 M 2-thenoyltrifluoroacetone in benzene, together with 10 ml of water. The Th is stripped from the organic phase with 2 N HNO_3 (10 ml) and the aq. phase is evaporated to dryness with HClO_4 to remove any organic material. Finally, the Th is extracted into HClO_4 (pH 2) and 0.5 ml of an ethanolic soln. of morin is added. The extinction of the complex is measured after 1 hr. at 412 m μ in a 1-cm cell with slit-width 0.03 mm.
W. J. BAKER

1918. Determination of elementary sulphur [in tissue extracts] by paper chromatography. A. Jakubovič and Ž. Procházka (Chem. Inst., Acad. Sci., Prague, Czechoslovakia). *Chem. Listy*, 1956, **50** (12), 2029-2031.—The paper-chromatography method has been found suitable for the micro-detection of sulphur in tissue extracts. Ethanol (96%) was used as solvent, and an ammoniacal soln. of AgNO_3 (0.1 N AgNO_3 - 5 N aq. NH_3 (1:1) with a soln. of $\text{Na}_2\text{S}_2\text{O}_3$ (10%) as detecting reagent. Photographed chromatograms were evaluated by photometric methods and the quantity was measured planimetrically from corresponding graphs. As little as 0.15 μg of S can be detected; Se and Te do not interfere.
J. ŽYKA

1919. The determination of inorganic phosphate and creatine phosphate in tissue extracts. R. F. Furchgott and T. de Gubareff (Dept. of Pharmacol., Washington Univ. Sch. of Med., St. Louis, Mo., U.S.A.). *J. Biol. Chem.*, 1956, **223** (1), 377-388.—The method of Fiske and Subbarow (*Brit. Abstr. A*, 1926, 443) for the determination of inorg. and org. phosphate is modified, so that inorg. phosphate and creatine phosphate can be determined successively on the same aliquot of tissue extract during a continuous run in a spectrophotometer. Inorg. phosphate is first determined at pH 2.3 in the presence of added CuSO_4 to increase greatly the rate of development of the reduced molybdophosphate colour. Concentrated acid is then added to hydrolyse the creatine phosphate, and the extra colour developed is a measure of this compound.
J. N. ASHLEY

1920. The separation of carbonyl compounds before blood-alcohol determination. III. E. Vidic (Inst. für gerichtl. u. soziale Medizin., Freie Univ., Berlin, Germany). *Arzneimittel-Forsch.*, 1956, **6** (12), 762-766.—Attempts were made to separate acetone bodies present in blood before the determination of ethanol by the method described previously (*cf. Anal. Abstr.*, 1955, **2**, 1276). Acetone could be removed completely by means of a strongly alkaline suspension of HgO , but slight loss of ethanol occurred. In the recommended method, carbonyl compounds are pptd. as the *p*-nitrophenylhydrazones after the addition of sodium tungstate soln. and dil. H_2SO_4 .
A. R. ROGERS

1921. Metabolites of salicylic acid in urine. Quantitative determination. S. L. Tompsett (Northern Gen. Hosp., Edinburgh, Scotland). *Clin. Chem.*, 1956, **2** (3), 166-169.—By means of single-dimension paper-chromatography the free salicylic acid, conjugated salicylic acid, and total (free and conjugated) gentisic acid are determined in urine. The Kawerau unit (*Biochem. J.*, 1951, **48**, 281) with a benzene-glacial acetic acid-water (2:2:1) system is used for the chromatography. The colours are developed with Folin-Ciocalteu reagent and read at 600 m μ .
H. F. W. KIRKPATRICK

1922. Persistence of reserpine action after the disappearance of drug from brain. Effect of serotonin. S. M. Hess, P. A. Shore and B. B. Brodie (National Heart Inst., Bethesda, Md., U.S.A.). *J. Pharmacol.*, 1956, **118** (1), 84-89.—A method for the assay of reserpine in tissues and plasma is included. The drug is isolated from alkaline biological material by extraction into heptane. It is then extracted into aq. H_2SO_4 and treated with selenous acid to convert it into a highly fluorescent derivative.
G. F. SOMERS

1923. The determination of N-butyl-N'-toluene-p-sulphonylurea [tolbutamide] in serum. H. Spingler and F. Kaiser (C. F. Boehringer u. Soehne G.m.b.H., Mannheim-Waldhof, Germany). *Arzneimittel-Forsch.*, 1956, **6** (12), 760-762.—In this spectrophotometric method for the determination of the oral antidiabetic agent tolbutamide (I) in serum, the absorption maximum at 228 m μ , for which $E_{1\text{cm}}^{1\%} = 492$, is used. Irrelevant absorption is corrected by a blank determination. *Procedure*—Freeze-dry the sample (1 ml). Stir the residue with ethyl acetate (3 ml) for 1 min., add N HCl (five drops), stir for 5 min. and allow to settle. Evaporate a 1-ml aliquot of the supernatant liquid

to dryness on a steam bath, dissolve in methanol (3 ml) and compare the extinction with that of pure methanol at 228 $m\mu$ and 280 $m\mu$, with 1-cm cells. Simultaneously carry out a blank determination on I-free serum (preferably from the same patient before the administration of I). If A and B are the extinction values in the presence and absence of I, respectively, then the extinction at 228 $m\mu$ due to I is given by $A_{228} - (A_{280} \cdot B_{228} / B_{280})$.

A. R. ROGERS

1924. Colorimetric determination of diphenyl in biological materials. R. B. Bruce and J. W. Howard (Hazleton Lab., Falls Church, Va., U.S.A.). *Anal. Chem.*, 1956, **28** (12), 1973-1975.—Diphenyl is nitrated in acetic acid soln. with conc. HNO_3 , the 4-nitrodiphenyl derivative is reduced and the resulting amine is coupled with N-(1-naphthyl)-ethylenediamine to give a purple dye whose extinction is measured at 570 $m\mu$. The diphenyl is extracted from biological material into CHCl_3 before this procedure. Recoveries of added diphenyl from blood and urine averaged 94 and 100%, respectively, over the approx. concn. range of 10 to 75 μg per 5 ml, and from faeces, 91% for the range 2.5 to 10 mg per 5 g.

G. P. COOK

1925. Determination of DDA [di-(p-chlorophenyl)-acetic acid] in urine using an ion-exchange resin. C. Cueto, A. G. Barnes and A. M. Mattson (U.S. Dept. of Health, Educ. and Welfare, P.O. Box 769, Savannah, Ga., U.S.A.). *J. Agric. Food Chem.*, 1956, **4** (11), 943-945.—A routine method is described for the determination of DDA, the metabolite excreted by animals and humans fed with DDT. *Procedure*—The urine sample (>100 ml) containing $<5 \mu\text{g}$ of DDA is heated for 1 hr. under reflux at 90° to 95° with 2 g of Amberlite IRA-400 (in OH or Cl form), followed, without cooling, by shaking for 1 hr. The urine is aspirated off, with a filter-stick, 50 ml of ethanolic acetic acid (200 ml of glacial acetic acid diluted to 1 litre with ethanol) is added, and the mixture is heated for 1 hr. under reflux and then filtered while hot. The residue is washed with the min. vol. (10 to 15 ml) of ethanol, and the combined filtrate and washings are diluted with ≈ 100 ml of water. The soln. is shaken thoroughly with exactly 50 ml of benzene, and, after being separated, the benzene layer is washed with water and dried with anhyd. Na_2SO_4 . To a 40-ml aliquot of the benzene solution in a test-tube is added 10 mg of stearic acid in 1 ml of benzene, and the solvent is removed by warming in a water bath in a current of air. The test-tube is washed down with 5 ml of ethanol, the solvent again removed, and the DDA determined in the residue by a modified Schechter-Haller method (Communicable Dis. Center, Tech. Development Lab., U.S. Publ. Health Service, Chem. Memorandum No. 1, 1st rev., 1953).

S. C. JOLLY

1926. Plasma fibrinogen determination. A rapid titration method. A. A. Rosenberg (Veterans Admin. Hosp., Albany, N.Y., U.S.A.). *Clin. Chem.*, 1956, **2** (5), 331-333.—Place 1 ml of normal saline in each of ten tubes (12 mm \times 75 mm); to the first add 1 ml of plasma (from oxalated blood), mix, transfer 1 ml to the second tube and continue the serial dilution. To each tube add one drop of 0.25% methylene blue. Add 0.2 ml of thrombin soln. (powdered thrombin, topical, 1000 units dissolved in 10 ml of water) to the first tube, shake gently for 2 sec. and repeat with each tube. Allow the tubes to stand undisturbed at room temp. for

5 min., add 2 ml of saline to each tube without shaking, and read at once the highest dilution that shows a definite clot (more clearly seen by retention of the dye in the clot giving two colour phases) and report as a titre. Titres of >64 , 64, and <64 indicate >0.2 , 0.1 to 0.2, and <0.1 g-% of fibrinogen, respectively. Abnormal bleeding may occur when the titre is 32 or less.

H. F. W. KIRKPATRICK

1927. Quantitative micro-estimation of formaldehyde in the presence of periodate and its application to the structural examination of carbohydrate phenylosazones. L. Hough, D. B. Powell and B. M. Woods (The Univ., Bristol, England). *J. Chem. Soc.*, 1956, 4799-4803.—The colorimetric determination of formaldehyde by means of phenylhydrazine and ferricyanide (Dowse and Saunders, *Anal. Abstr.*, 1956, **3**, 2309) has been adapted for use in periodate oxidations. Complete removal of periodate was effected by pptn. as the Ba salt in the presence of NaHCO_3 .

O. M. WHITTON

1928. The determination and excretion of adrenaline and noradrenaline in urine. E. Pitkanen (Dept. of Med. Chem., Univ. of Helsinki, Finland). *Acta Physiol. Scand.*, 1956, **38**, Suppl. 129 (in English).—*Procedure*—Dilute a 24-hr. specimen of urine to 1.5 litres, transfer 12.5 ml to a separating funnel, with a tight glass-wool layer at the bottom, and add 20 mg of ascorbic acid, 0.5 ml of 50% Na citrate, 1.5 g of Al_2O_3 (chromatographic) and H_2O to 50 ml. Adjust the pH to 8.5 with 2 N NaOH and shake vigorously for 5 min., allow to stand for 4 min. and decant the supernatant liquid; wash the Al_2O_3 with 50 ml of H_2O by thorough shaking, allow to stand for 3 min., decant the supernatant liquid, then remove the remainder of the H_2O by suction. Shake the Al_2O_3 with 5 ml of N H_2SO_4 , allow the particles to settle, transfer 1 ml to a test-tube and shake with 1 ml of redist. butyl alcohol; allow the emulsion to break down, remove and discard the alcohol layer and adjust the pH to 6.3 by adding 14.2 ml of 2 N Na acetate soln. Place 5-ml aliquots of this soln. in each of three tubes and add, respectively, 1.5 ml of H_2O ; 0.5 ml of H_2O and 1 ml of adrenaline soln. (25 μg per 100 ml); and 0.5 ml of H_2O and 1 ml of noradrenaline soln. (25 μg per 100 ml). To each of the three tubes add 5 mg of freshly washed MnO_2 , shake for 3.5 min. and centrifuge. Take three samples of 2 ml from each tube; to the first (from each tube) add 0.4 ml of 5 N NaOH containing 100 mg-% of ascorbic acid (for total fluorescence). To the second add 0.36 ml of 5 N NaOH, followed 45 sec. later by 0.04 ml of 1% ascorbic acid (fluorescence due to adrenaline). To the third add 0.36 ml of 5 N NaOH, followed 4 min. later by 0.04 ml of 1% ascorbic acid soln. (blank fluorescence). Conjugates can be hydrolysed by acidifying the urine to pH 1 and heating in boiling water for 20 min.; the estimation is as above. The fluorescence is read with Corning 5860 as primary and 3389 as secondary filter (both double thickness) in a sensitive fluorimeter (Farrand). The recovery of noradrenaline averaged 69.5% and of adrenaline 76%. The test is of diagnostic value in pheochromocytoma when the excretion of these substances totals 200 to 1000 μg per day (normal excretion up to 100 μg per day).

H. F. W. KIRKPATRICK

1929. Determination of α -tocopherol in human blood by paper chromatography. L. Delmas. *Compt. Rend.*, 1956, **242** (21), 2595-2598.—The sample (serum or blood) was saponified in the

presence of pyrogallol, and the unsaponifiable matter was extracted with light petroleum. The solution was dried and dissolved in a known amount of light petroleum or acetone. For the chromatographic separation, purified spermaceti, mixed with a ferric salt of undecic acid, was used for the stationary phase, and aq. acetone (25% of water) for the mobile phase. The stains due to the α -tocopherol were sharply defined. Quantities of 0.4 to 0.9 μ g of α -tocopherol were accurately determined and 0.06 μ g was detectable; a 0.02- μ g difference between spots was distinguishable. In spite of the small samples used (0.5 to 0.05 ml of serum), and the preponderance of other unsaponifiables, the α -tocopherol was readily separated and further purification was unnecessary. The time required for the determination was about 2.5 hr. Samples of differing lipid content, and taken from subjects of various ages and both sexes, were used, and it was also established that keeping the serum for several weeks at -20° left the α -tocopherol unchanged. In normal subjects the amount of α -tocopherol usually found was 8 to 10 mg per 1000 ml of serum.

J. F. P. H. GREENE

1930. The determination of acid aminopolysaccharide in urine. N. DiFerrante and C. Rich (Rockefeller Inst. Med. Res., New York, U.S.A.). *J. Lab. Clin. Med.*, 1956, **48** (3), 491-494.—Urinary acid aminopolysaccharide (I) is determined by pptn. with cetyltrimethylammonium bromide, separation of the ppt. and determination of its glucuronic acid content. The standard deviation is 4.55%. The method also gives quant. recovery of sodium heparinate and hyaluronate and of chondroitinsulphate. Significant differences were found for I according to age and sex. *Procedure*—To 30 ml of urine (24-hr. sample, diluted, if necessary, to sp. gr. <1.020 and adjusted to pH 5 with 2 N HCl) in a 40-ml conical centrifuge tube add 1 ml of 2.5% aq. cetyltrimethylammonium bromide. Mix, allow to stand overnight at 2° and centrifuge at room temp. for 15 min. at 2000 g. Decant the supernatant liquid, drain by inverting the tube for 1 min., wash the ppt. twice by stirring with 30 ml of 95% ethanol (saturated with NaCl) and centrifuging. Suspend the ppt. in 1.5 ml of water containing two drops of 0.1 N NaOH. Transfer quant. to a 5-ml or 10-ml calibrated flask (according to the amount of ppt.) and centrifuge to remove any undissolved matter. Determine the glucuronic acid content on 1 ml of the solution by the carbazole method of Dische (*Brit. Abstr. C*, 1947, 92) and express the result for I as glucuronic acid.

W. H. C. SHAW

1931. Oscillographic study of the Brdička polarographic filtrate reaction. V. Kalous and P. Valenta (Inst. Phys. Chem., Charles' Univ., Prague, Czechoslovakia). *Chem. Listy*, 1956, **50** (10), 1654-1656.—The Brdička polarographic filtrate reaction (*Research*, 1947, **1**, 25), commonly used for diagnostic purposes, can also be carried out oscillographically. This method is very rapid and suitable for routine analysis. The detailed procedure and a comparison of polarographic and oscillographic measurements are included.

J. ZÝKA

1932. A specific spectrophotometric assay for flavinadenine dinucleotide. C. DeLuca, M. M. Weber and N. O. Kaplan (McCollum-Pratt Inst., Johns Hopkins Univ., Baltimore, Md., U.S.A.). *J. Biol. Chem.*, 1956, **223** (1), 559-567.—A rapid and specific spectrophotometric method is described,

which is applicable in the presence of flavinadenine mononucleotide and other flavins. It involves coupling the D-amino-acid apo-oxidase to the lactic dehydrogenase system in the presence of catalase. This method, which accurately determines 0.15 μ g of flavinadenine dinucleotide, can also be used to detect D-amino-acid oxidase in tissues.

J. N. ASHLEY

1933. The separation of sphingolipids by adsorption chromatography. B. Weiss (Dept. of Biochem., N.Y. State Psychiatric Inst., New York, U.S.A.). *J. Biol. Chem.*, 1956, **223** (1), 523-534.—A chromatographic method is described for the separation of the sphingolipids of the central nervous system, by gradient elution with CHCl_3 and methanol from a silicic acid column.

J. N. ASHLEY

1934. Paper chromatography of phospholipids. G. Rouser, G. V. Marinetti, R. F. Witter, J. F. Berry and E. Stotz (Dept. of Biochem., Univ. of Rochester, New York, U.S.A.). *J. Biol. Chem.*, 1956, **223** (1), 485-497.—Many useful lipid separations are effected on non-impregnated filter-paper by the use of mixtures of lutidine and acetic acid with alcohols or chloroform. The factors that affect the mobility of phospholipids on paper are enumerated and discussed.

J. N. ASHLEY

1935. Reaction of amino acids with carbon disulphide. V. Paper chromatography and electrophoresis of carboxydithiocarbamates. B. Zahradník and V. Koblík (Inst. Hyg. and Ind. Diseases, Prague, Czechoslovakia). *Chem. Listy*, 1956, **50** (10), 1649-1651.—The reaction of 17 amino acids with CS_2 and the possibility of the chromatographic and electrophoretic separation of the formed carboxydithiocarbamates were studied. Mixtures of ethanol-butanol-0.05 M $\text{Na}_2\text{B}_4\text{O}_7$ (10:50:40); butanol-pyridine-0.05 M $\text{Na}_2\text{B}_4\text{O}_7$ (50:30:30); and propanol-aq. NH_3 (25%)-0.05 M $\text{Na}_2\text{B}_4\text{O}_7$ (70:5:25) were used as solvents. By using a paper saturated with 0.05 M $\text{Na}_2\text{B}_4\text{O}_7$, the chromatographic separation of 7 to 8 deriv. of amino acids with CS_2 was possible. The corresponding R_F values are presented.

J. ZÝKA

1936. A manometric method for quantitative estimation of amino acids. W. Gerok and H. D. Waller (Med. Klinik, Univ. Marburg, Germany). *Klin. Wochschr.*, 1956, **34** (47-48), 1284-1288.—The amino acids are oxidised by chloramine T to yield an equimolecular proportion of CO_2 . Addition of formaldehyde prevents oxidation of NH_3 to N. *Procedure*—Amino-acid soln. (1 ml containing 1 to 4 μ moles) is mixed with 0.4 ml of 0.24 M citric acid-phosphate buffer (pH 3.0) and 0.2 ml of 35% formaldehyde soln. in the Warburg apparatus at 37° . Freshly prepared 0.2 M chloramine T soln. (0.2 ml) is introduced into the apparatus, allowed to warm to 37° and is then added to the amino-acid mixture. The increase in pressure is read at 30, 40, 50 and 60 min. The mean value is calculated and, after correction for the blank, is converted to the amino acid by a factor.

H. F. W. KIRKPATRICK

1937. Quantitative determination of phenylalanine on paper chromatograms. A. E. Pasička and J. F. Morgan (Dept. of Nat. Health and Welfare, Ottawa, Canada). *Anal. Chem.*, 1956, **28** (12), 1964-1966.—Phenylalanine can be determined in the presence of 19 other amino acids by utilising the characteristic blue colour formed by it when ninhydrin-developed paper chromatograms are treated with dil. NaHCO_3 .

soln. The ninhydrin colours of the other amino acids can be removed from the strip by water washing without eluting the phenylalanine colour; this is extracted into *n*-butanol and is measured absorptiometrically at 600 m μ . Recoveries of phenylalanine were $\geq 95\%$ in the range 30 to 50 μ g per ml. G. P. COOK

1938. The spectrophotofluorimetric determination of tryptophan in plasma and of tryptophan and tyrosine in protein hydrolysates. D. E. Duggan and S. Udenfriend (Lab. of Chem. Pharmacol., Nat. Heart Inst., U.S. Dept. of Health, Bethesda, Md., U.S.A.). *J. Biol. Chem.*, 1956, **223** (1), 313-319.—Ultra-violet fluorescent spectra of tryptophan and tyrosine are used for the determination of these amino acids in protein hydrolysates. The assay is rapid, simple and specific, and the results agree with those obtained by other methods. A very sensitive spectrophotofluorimetric method is described for the determination of free tryptophan in plasma. It is much simpler than a bio-assay. J. N. ASHLEY

1939. Quantitative electrophoresis of serum proteins on paper. M. Wurm and F. H. Epstein (Dept. of Pathol., St. Joseph Hosp., Burbank, Calif., U.S.A.). *Clin. Chem.*, 1956, **2** (5), 303-319.—The protein fractions of serum are more correctly evaluated after densitometric measurement of the stained paper-electrophoretic pattern by assuming that the extinction is proportional to the log. of the protein concn., as Beer's law is not applicable. This relationship gives results in close agreement with those given by moving-boundary electrophoresis. H. F. W. KIRKPATRICK

1940. Electrophoretic analysis of blood serum in acetate buffers. V. Kalous and J. Poláček (Inst. Phys. Chem., Charles' Univ., Prague, Czechoslovakia). *Chem. Listy*, 1956, **50** (10), 1656-1659.—Since the mobility of the M-2 component of blood serum (Mehl, Golden and Wenzler, *Proc. Soc. Exp. Biol. Med.*, 1949, **72**, 110) at various pH values had not been measured, the authors analysed blood-serum samples containing an increased amount of M-2 component as well as of M-1 (mucoprotein) in acetate buffer soln. pH 4.2 to 5.2. The results obtained for mobility and iso-electric point of M-2 are reported. J. ŽÝKA

1941. Alcian blue and colloidal iron staining methods adapted to filter-paper electrophoresis. L. Feeney and W. K. McEwen (Francis I. Proctor Foundation for Research in Ophthalmology, Univ. California, San Francisco). *Stain Tech.*, 1956, **31**, 135-139.—Small sheets of Whatman No. 1 filter-paper were moistened with various soln. normally used in electrophoresis, such as borate buffer, pH 8.6, ionic strength (μ) 0.05; barbitone buffer, pH 8.6, μ 0.16; phosphate buffer, pH 7, μ 0.16, or pH 7.8, μ 0.13. Samples of 0.5 or 1 μ l were spotted on to the moistened filter-paper, which was subsequently dried before staining. Samples from commercial and natural sources were tested; those from commercial sources were hyaluronic acid, heparin, chondroitinsulphate, ovomucoid, and gastric mucin, while blood serum, saliva, tears, vitreous and aq. humour were from natural sources. Alcian blue [1 g of Alcian blue 8GS in 100 ml of 95% ethanol, diluted (1:9) with 2% acetic acid (Novelli, *Experientia*, 1953, **9**, 34)] was found to be a good general stain for mucoproteins on filter-paper that had been immersed in 95% ethanol, drained and air-dried. Blood and aq. humour are

not stained by this method, but do respond to staining with colloidal iron. P. HAAS

1942. Quantitative nephelometric micro-determination of α -globulins in serum and cerebrospinal fluid. A. Saifer and M. C. Zymaris (Isaac Albert Research Inst., Jewish Chronic Disease Hosp., Brooklyn, N.Y., U.S.A.). *Clin. Chem.*, 1956, **2** (3), 195-213.—The total α -globulins in serum and cerebrospinal fluid may be determined by the turbidity produced with benzyldimethyloctadecylammonium chloride (Octab) or the corresponding cetyl compound (Cetol). Full expt. details of the procedures are given. H. F. W. KIRKPATRICK

1943. Paper chromatography in steroid determination. L. M. Reineke (The Upjohn Co., Kalamazoo, Mich., U.S.A.). *Anal. Chem.*, 1956, **28** (12), 1853-1858.—The application of paper chromatography to the identification and quant. determination of steroids obtained from microbiological and chemical transformations is discussed. An indication of the possible structure of an unknown steroid can be obtained by means of u.v. absorption, chemical tests and mobility measurements in a variety of solvent systems. Data for 121 steroids are listed. A quant. spectrophotometric method is described for progesterone and 11 α -hydroxyprogesterone. This involves paper-chromatographic separation of the steroids, extraction of the cut zones with solvent, and measurement at 224 and 242 m μ . Recoveries of the steroids averaged $\approx 100\%$. G. P. COOK

1944. Cholesterol in serum and lipoprotein fractions. Its measurement and stability. J. T. Anderson and A. Keys (Lab. of Physiol. Hygiene, Univ. of Minnesota, Minneapolis, U.S.A.). *Clin. Chem.*, 1956, **2** (3), 145-159.—A method is given for determining cholesterol (I) in serum by hydrolysing with alcoholic KOH at 37°, extracting with light petroleum, removing the solvent and measuring the colour given by the dry residue with Liebermann-Burchard reagent. This method is applied to the estimation of I in the α - and β -lipoprotein fractions separated either by paper electrophoresis or by an adaptation of the cold ethanol fractionation procedure of Cohn. In serum stored at -20°, I is stable for at least five years; in lyophilised serum no change in I was observed after many months at room temp. On dried paper-electrophoresis strips, I is stable for many weeks at room temp.

H. F. W. KIRKPATRICK

1945. Simplified rapid technique for the extraction and determination of serum cholesterol without saponification. J. J. Carr and I. J. Drechter (Mt. Sinai Hosp., New York, N.Y., U.S.A.). *Clin. Chem.*, 1956, **2** (5), 353-368.—To 0.2 ml of serum in a centrifuge tube add 0.8 ml of glacial acetic acid, mix, and allow to stand for 1 to 2 min. Treat a second 0.2 ml of serum for the serum blank and 0.2 ml of water for the reagent blank similarly. To each tube add 4 ml of acetic anhydride, mix by a rotary movement and centrifuge at 2000 r.p.m. for 5 min. Decant the clear supernatant liquids, add 1 ml of glacial acetic acid to the serum blank only and set this aside for photometric reading. To the test sample and reagent blank add 1 drop of dehydrating reagent [H_2SO_4 -glacial acetic acid, 1:1 (v/v), diluted with an equal vol. of glacial acetic acid] and mix, and if the soln. does not become hot within 1 to 2 min. add one further drop, but no more. Place the tubes in a water bath at 25° and after 5 to 10 min. pipette 1 ml of H_2SO_4 -

glacial acetic acid [1:1 (v/v)] directly into the soln. allowing 1-min. intervals between the tubes. Read the colours, and that of the serum blank, at 620 $m\mu$ after 20 min. To standardize, dilute 0.1 to 0.5-ml aliquots of standard cholesterol soln. (200 mg per 100 ml in glacial acetic acid) to 0.8 ml with glacial acetic acid, add 0.2 ml of water and treat as the test sample. By this method cholesteryl esters yield the same colour intensity as the free sterol.

H. F. W. KIRKPATRICK

1946. Urinary oestrogens in pregnancy. Improved method for their determination in humans. R. M. Anker (Dept. of Obstr. and Gynecol., Univ. of Colorado, Denver, U.S.A.). *Clin. Chem.*, 1956, **2** (3), 184-187.—The urine is acidified with H_3PO_4 to pH 2, saturated with *n*-butanol and extracted in a special type of liquid-liquid extractor with butanol (5 \times 50 ml). The combined butanol extracts are boiled under reflux, 15 ml of conc. HCl per 100 ml of extract is added through the condenser and the boiling is continued for 1 hr. The butanol is neutralised with conc. aq. NH_3 and distilled off in steam. The resulting aq. soln. is extracted with toluene and the oestrogens are assayed by the method previously described (*Anal. Abstr.*, 1955, **2**, 1640). Hydrolysis of the conjugated oestrogens in butanol medium is accompanied by less destruction than in aq. soln. H. F. W. KIRKPATRICK

1947. Spectrophotometric determination of Δ^4 -3-ketosteroids. D. Abelson and P. K. Bondy (Yale Univ. Sch. of Medicine, New Haven, Conn., U.S.A.). *Anal. Chem.*, 1956, **28** (12), 1922-1924.— Δ^4 -3-Ketosteroids react with potassium *tert*-butoxide in *tert*-butyl alcohol to produce a yellow colour with absorption max. at 260 and 385 $m\mu$; the extinction at 385 $m\mu$ varies in accordance with Beer's law. Oestril, oestradiol and oestrone show max. at 250 and 310 $m\mu$. The sensitivity is 1 to 2 μg of steroid, and the standard deviation is $\pm 2.5\%$ for a single steroid. G. P. COOK

1948. A simplified blue tetrazolium reaction. R. O. Recknagel and M. Lilteria (Western Reserve Univ. Sch. Med., Cleveland, Ohio, U.S.A.). *J. Lab. Clin. Med.*, 1956, **48** (3), 463-468.—From a study of the reaction conditions in the colorimetric determination of adrenocortical steroids with blue tetrazolium [3:3'-(3:3'-dimethoxy-4:4'-diphenyl-ene)-di-(2:5-diphenyltetrazolium chloride)] (I) the simple rapid method described is found to give reproducible results and rectilinear calibration, and to have a satisfactory working range of 10 to 50 μg of corticosterone. *Reagents*—(i) Redistilled absolute ethanol twice over alkaline I. (ii) Recrystallise I from ether and prepare a solution in (i) containing 0.25 mg per ml. (iii) Prepare 0.03 N ethanolic NaOH by dilution of 6.0 N aq. NaOH with (i). Use within 1 hr. *Procedure*—Place known amounts of the steroids in methanol, or washed $CHCl_3$ extracts of enzyme degradation reactions (*Proc. Soc. Exp. Biol. Med.*, 1955, **89**, 153), in matched colorimeter tubes (1.3 cm \times 10 cm), and evaporate the solutions to dryness in a gentle stream of air which has been passed through activated carbon and absorbent cotton. Add 2.0 ml of (ii) to the residue and then 1.0 ml of (iii). Allow max. colour to develop at room temp. (usually 30 to 50 min. according to the steroid under test) and read the extinction at 525 $m\mu$. W. H. C. SHAW

1949. Urinary glucocorticoid excretion. A. Moxham and J. D. N. Nabarro (Inst. of Clin. Research, Middx. Hosp., London, England). *J. Clin. Path.*,

1956, **9** (4), 351-357.—17-Hydroxycorticosteroids were determined in urine by the method of Reddy *et al.* (*Metabolism*, 1952, **1**, 511), 56% H_2SO_4 being used for colour development (Smith *et al.*, *J. Clin. Endocrinol.*, 1954, **14**, 336). The *n*-butanol was purified by adding phenylhydrazine hydrochloride (2 g to 2 litres), acidifying with a few drops of glacial acetic acid, allowing to stand for 7 days and then distilling twice, collecting the fraction boiling at 117°. Photometric instruments with filters were found to be unsuitable for use with this method. 17-Ketosteroids were determined either indirectly after sodium bismuthate oxidation (*Lancet*, 1953, **i**, 1276) or directly with sodium borohydride (*Biochem. J.*, 1955, **60**, 453), the methods being modified by adopting a larger scale extraction with benzene as solvent similar to that of the M.R.C. method (*Lancet*, 1951, **ii**, 585).

H. F. W. KIRKPATRICK

1950. Measurement of enzymatic amylolytic activity. Group A. II. Methods depending on determination of decrease in viscosity of starch paste. (Viscosimetric determination of amylase.) H. Wildner and G. Wildner (Ireks Forschungsinstit. für Gärungswissenschaft, Kulmbach, Germany). *Brauwissenschaft*, 1956, **9** (11), 296-302.—Descriptive reviews are given of the construction and operation of several types of viscometer as modified for the determination of the decrease in viscosity of starch soln. due to amylolytic activity. The prep. of the appropriate starch soln. is described, and examples are given of the applications of the methods to extracts of barley and malt and other diastatic prep.

III. Methods depending on the determination of the turbidity-clearance of glycogen or starch solution (nephelometric determination of amylases). H. Wildner and G. Wildner. *Ibid.*, 1956, **9** (12), 310-313.—Glycogen soln. (91 ml, 0.3%) [prepared from the liver of a freshly killed rabbit, given 50 ml of glucose (50% soln.) 2 to 3 hr. previously] is placed in each of a series of cylinders (100 ml), and *M*/3 phosphate buffer (1 to 3 ml) and 0.1 N NaCl soln. (1 ml) are added and mixed; the temp. is kept at $37^\circ \pm 0.05^\circ$. Amylase soln. (5 ml of 0.5 to 3.0 ml of human saliva diluted to 100 ml) at the same temp. is added and mixed. After 30 sec. a sample (15 ml) is taken out of each cylinder and placed in a dry flask in ice water. Tests are made after 10 or 15 min. The turbidity, not recognisable at 0° , changes with time and nephelometric examination is soon possible. The results are calculated from the equation $c_1 = 100 \times h/h_1$, where c_1 is the concn. of the cleavage product, and h and h_1 are the nephelometric values for the original soln. and the cleavage product, respectively. A standard glycogen curve is prepared. P. S. ARUP

S.C.I. ABSTR.

1951. The estimation of true lipase in small intestinal contents. H. G. Sammons, A. C. Frazer and M. Thompson (Dept. of Pharmacol., Univ. of Birmingham, England). *J. Clin. Pathol.*, 1956, **9** (4), 379-380.—Add 1 ml of olive oil, previously de-acidified by passage through an alumina column, to 5 ml of phosphate buffer soln. (pH 7.8) containing 0.5% of bile salts (Difco No. 3) in a 50-ml stoppered conical flask. Add 0.1 ml of duodenal juice and shake in a "Microid" flask shaker at 750 vibrations per min. for 30 min., clamping the flask so that the lower half is in water at 37° . Add 5 drops of conc. HCl and extract the mixture with 20 ml of benzene, shaking by hand for 1 min. To 10 ml of the benzene layer add 1 ml of ethanol and titrate with 0.05 N

tetramethylammonium hydroxide in ethanol between the yellow and green - blue end-points, with thymol blue (0.1% in ethanol) as indicator. A unit of lipase is taken as the no. of ml of 0.1 N alkali required to neutralise the fatty acids under the conditions of the test. Normal values are 2 to 6 units per 0.1 ml of duodenal juice, irrespective of age. The speed of the shaker was found to be a critical factor, as below 700 vibrations per min. the acid liberated decreased with decreasing speed.

H. F. W. KIRKPATRICK

See also Abstract 1968.

Drugs

1952. Application of polarographic analysis to the control of pharmaceuticals. I. Wilczyńska (Chem. Dept., Inst. of Drugs, Warsaw). *Chem. Anal., Warsaw*, 1956, **1** (2-3), 106-111.—The advantages of polarographic analysis in pharmaceutical work are discussed. The following pharmaceutical substances were found to be suitable for polarographic testing—formaldehyde, formic acid, isoniazid, nicotinamide, methylhydroxylamide of nicotinic acid, pteroylglutamic acid, indigo carmine, morphine, codeine, dihydrocodeine, dihydrocodeinone, dihydroxycodeinone, quinine, diphenylethylamide of nicotinic acid, salicylazosulphanilamidopyridine, chrysoidine and pteroyltriglutamic acid.

K. F. SPOREK

1953. Note on the identification of alkaloids by paper chromatography. G. Nadeau (Hôpital St. Michel-Archange, Mastai, Quebec, Canada). *Clin. Chem.*, 1956, **2** (5), 347-352.—*n*-Butanol or *iso*-butyl alcohol is shaken several times daily during three days with ethanol - glacial acetic acid - water (10:1:5) and separated, and the butanol phase is employed as solvent. A solution of the alkaloid in this solvent is applied to the bottom of a sheet of No. 1 or No. 4 Whatman paper (22 cm × 28 cm), which is then rolled into a cylinder and stapled and kept in an atmosphere of the aq. phase for 2 to 3 hr.; it is then dipped into the solvent in a closed container. When the solvent has risen to about 2 cm from the upper edge, the paper is dried at room temp. in a current of air and sprayed with potassium iodoplatinate soln. (1 g of platonic chloride dissolved in 10 ml of water, mixed with 250 ml of 4% KI and made up to 500 ml with water). Better resolution of the spots may be obtained if the paper is evenly sprayed, after applying the alkaloid soln., with a citrate - phosphate buffer soln. of pH 4.0. The position and colour of the spot are diagnostic of the alkaloid. The method appears to be especially suitable for the detection of small amounts of alkaloid (e.g., morphine) in biological material.

H. F. W. KIRKPATRICK

1954. Determination and extraction of alkaloids in crude drugs and galenicals with the aid of ion-exchange resins. W. Kamp (Lab. voor Artesnijbereidkunde, Amsterdam, Holland). *Pharm. Weekbl.*, 1957, **92** (1), 1-24 (partly in English).—A method for the assay of total alkaloids of belladonna, hyoscyamus and nux vomica by the use of a strong cation-exchange resin IMAC-C22 has been devised. A rapid method was found for the determination of hydrastine in hydrastis rhizome with the same resin. To determine the strychnine content of nux vomica, the soln. of the total alkaloids isolated with IMAC-

C22, after nitration of brucine, was percolated through another similar column. For the isolation and assay of morphine in opium, a strong anion-exchange resin Amberlite IRA-400 was used. By combining the two resins, two separations were effected. (i) The alkaloids of *ipeacacuanha* root were separated into phenolic (cephaline) and non-phenolic alkaloids (emetine), and (ii) the six principal alkaloids of opium (codeine, morphine, narceine, narcotine, papaverine and thebaine) were separated. It may thus be possible to determine several alkaloids in crude drugs and galenicals by using a cation or a cation and anion resin, without preliminary purification.

P. HAAS

1955. Paper-chromatographic determination of alkaloids in mydriatic ointments. A. Del Pozo, J. M. Pla and F. Suñer. *Galenica Acta, Madrid*, 1955, **8**, 27-42.—Alkaloids were extracted from 2-g samples with 5 or 10 ml of ether. The extract was shaken with 20 ml of water and 5 ml of N HCl for 20 min., and twice with 5 ml of N HCl. The aq. layer was made alkaline with aq. NH₃ and shaken with ether - chloroform (1:2) for 20 min., treated with Na₂SO₄, filtered, the filter and ppt. washed with ether - chloroform, and the soln. evaporated to yield the alkaloids. These were taken up in *iso*-propyl alcohol and one drop was applied to Whatman No. 1 paper that had been treated with 0.2 M KH₂PO₄ - K₂HPO₄ at pH 6.7 (Na interferes). Amyl alcohol was used as the developer and Jentsch reagent for alkaloid identification. The spot characteristic for atropine is strong orange, long with sharp border, optimum concn. 40 µg, R_F 0.16 at 5° and 0.21 at 15°; ethylmorphine, red, round, 80 µg, R_F 0.40, 0.51; hyoscyne, red, round, 40 µg, R_F 0.55 at 15°; cocaine, shape of spot not uniform, borders undefined, colourless, 40 µg, R_F 0.68, 0.73; quinine, big oval spot in red circle with colourless halo, if concn. is more than 30 µg, R_F 0.78 at 15°; ethylhydrocupreine 40 µg, R_F 0.88 at 15°.

CHEM. ABSTR.

1956. Alkalimetric determination of salts of organic bases after precipitation in the form of tetraphenylborides. II. Alkaloid salts and salts of organic bases of pharmaceutical interest. J.-A. Gautier, J. Renault and F. Pellerin (Fac. de Pharm., Paris, France). *Ann. Pharm. Franç.*, 1956, **14** (5), 337-340.—To the amine or its salt (0.25 milliequiv.) are added 1% acetic acid (to pH 4.5) and five drops of AlCl₃ soln. The mixture is heated to between 40° and 50° and a 1% aq. soln. of Na tetraphenylboron is added, dropwise. After 30 min. the ppt. is collected in an Allihn tube and washed with 1% acetic acid. The ppt. is washed from the filter with acetone, evaporated to dryness and completely dried at 60°. The ppt. is then dissolved in 10 ml of anhyd. acetic acid and titrated with 0.05 N HClO₄ in acetic acid, with methyl violet as indicator. Some 30 pharmaceutically important bases have been determined in this way. Those bases strong enough to form salts in aq. soln. form 1:1 salts with tetraphenylboron ions; quinine forms a salt with 2 mol. of tetraphenylboron. The N groups of *p*-aminobenzoic acid, indole and amides will not form such ppt., but the first of these may be titrated in acetic acid. Physostigmine behaves as a monobasic compound with Tropaeolin OO as indicator, but as a dibasic one to methyl violet; the Tropaeolin gives a sharper end-point.

E. J. H. BIRCH

1957. **Some components of gas phase of cigarette smoke.** (I). J. S. Osborne, S. Adamek and M. E. Hobbs (Duke Univ., Durham, N.C., U.S.A.). *Anal. Chem.*, 1956, **28** (2), 211-215.—By a combination of i.r. compensation absorption and mass spectral procedures applied to samples of the gas phase previously fractionated at low temp. its composition has been quant. determined as regards all the major constituents and a considerable number of minor components.

(II). R. J. Philippe and M. E. Hobbs. *Ibid.*, 1956, **28** (12), 2002-2005.—Earlier studies described by Osborne *et al.* (see Part I above) have been extended. Two additional tobacco compositions were analysed by an i.r. absorption technique and compounds that were not previously reported have been identified and quant. determined. These included butane, isobutylene, benzene, toluene, furan and 2-methylfuran. Absorption-band data for the compounds identified and for compounds not yet identified are listed.

N. E.

G. P. Cook

1958. **Nicotinic and glutamic acids, nicotinamide, and glutamine in cigarette-tobacco smoke.** D. A. Buyske, J. M. Flowers, jun., P. Wilder, jun., and M. E. Hobbs (Dept. of Chem., Duke Univ., Durham, N. Carolina, U.S.A.). *Science*, 1956, **124**, 1080.—Glutamic acid and glutamine were detected by chromatographing a nitrogenous, ninhydrin-positive, amphoteric fraction of collected smoke on Dowex-50 (8% cross-linked, 200 to 400 mesh, H form), eluting six separate ninhydrin-positive fractions with 2 N HCl and comparing the fractions directly with authentic amino acids in different paper-chromatography systems. Nicotinic acid and nicotinamide were detected and determined by dissolving smoke, collected in solid CO₂-acetone traps, in ether, extracting three times with an equal vol. of 2% HCl, adjusting the acid layer to pH 10.0 with NaOH and extracting twice with an equal vol. of ether. The aq. layer was neutralised and concentrated to small vol. This soln. was chromatographed on Whatman No. 1 paper in Na citrate buffer (pH 6.3) and the *R_F* values were determined by developing a colour reaction with *p*-aminobenzoic acid in an atm. of cyanogen bromide. Quantitative determinations were made with *Lactobacillus arabinosus*.

H. F. W. KIRKPATRICK

1959. **Microbiological determination of biotin in drugs and natural materials by means of *Lactobacillus arabinosus*.** S. Tuszyńska, K. Myszkowska, W. Woźniak and K. Lewandowska (The Drug Inst., Warsaw). *Chem. Anal., Warsaw*, 1956, **1** (1), 93-98.—The simple method described is based on the Wright and Skeggs technique (*Proc. Soc. Exp. Biol. Med.*, 1944, **56**, 14607); millimicrogram quantities of biotin can be determined. *Procedure*—To each of a series of test-tubes add 5 ml of the medium soln. and quantities of biotin ranging from 0 to 5 μ g. Dilute to 10 ml with water, stopper the tubes and sterilise for 15 min. under pressure. After cooling, add to each tube one drop of the *L. arabinosus* culture and incubate the mixture at 30° for 24 to 72 hr. Determine the amount of lactic acid produced by titration with alkali.

K. F. SPOREK

1960. **Chemical determination of methionine in commercial preparations.** I. Eiichi Hiraoka. *Bull. Nat. Hyg. Lab., Tokyo*, 1955, (73), 69-74.—The nitroprusside method for the determination of methionine (I) is applied to commercial preparations

containing I and vitamins. A 20% HCl soln. is most satisfactory in the colour-developing process and for colour stability (up to 60 min.). Cysteine, cystine, thiourea and thioglycolate (0.01 to 0.005%) do not interfere. With commercial tablets of I, the recovery was 98 to 100.2%. *Procedure*—Grind the specimen, extract with water and filter; to 5 ml of the filtrate containing 0.2 to 1.5 mg of I add 1 ml of 5 N NaOH and 1 ml of 1% sodium nitroprusside, set aside for 10 min., add 3 ml of 20% HCl, and, 30 min. later, determine the extinction coeff. at 510 m μ with a S₈₃ filter.

II. Eiichi Hiraoka and Yukio Nakaji. *Ibid.*, 1955, (73), 75-78.—Contaminating thiamine can be eliminated from I by adsorption on zeolite or Japanese acid clay. Ascorbic acid is not completely removed by charcoal or Norite treatment since they adsorb I, too.

III. Eiichi Hiraoka, Yukio Nakaji and Shuntaro Ogawa. *Ibid.*, 1955, (73), 79-80.—The improved nitroprusside method is applied to commercial preparations of I for injection and tablets of I with satisfactory results.

CHEM. ABSTR.

1961. **Determination of the biological effectiveness of anthelmintics of the male fern type.** K. Jentzsch and H. Ronge (Pharmakog. Inst., Univ. Wien). *Arzneimittel-Forsch.*, 1956, **6** (11), 639-647.—A biological method is described for the assay of preparations of male fern, hexylresorcinol being used as the standard. The method is based on the toxicity to worms of the species *Eisenia foetida* in a three-point assay procedure based on the probit mortality. The results obtained showed that the chemical determination of crude filicin was not a reliable index of the biological activity.

G. F. SOMERS

1962. **The photometric estimation of penicillin with *p*-dimethylaminobenzaldehyde.** T. Gašper, J. Kolšek and M. Perpar (Inst. für organ. Chem., Univ. Ljubljana, Yugoslavia). *Z. anal. Chem.*, 1957, **154** (2), 98-102.—Penicillin is subjected to acid hydrolysis; one of the products of this process gives a colour reaction with *p*-dimethylaminobenzaldehyde, which has been used as the basis of a photometric method for the determination of penicillin. Beer's law applies for concn. of penicillin up to 0.08 mg per ml, and as little as 0.01 mg of penicillin per ml may be quantitatively determined.

M. F. C. LADD

1963. **Quantitative determination of prednisolone and prednisone.** J. B. Jensen (Specialitetskontrollen, Brønshøj, Copenhagen, Denmark). *Dansk Tidsskr. Farm.*, 1956, **30** (11), 293-301.—Prednisolone (I) and prednisone (II) yield semicarbazones which show identical u.v. absorption spectra of the same intensity, with maxima at 242 and 292 m μ . Rough estimates of contents of hydrocortisone in I or of cortisone in II can be formed from the extent of displacements of these maxima. The determination of I or II with an error $\pm 3\%$ is based on the measurement of the absorption of the reaction product with semicarbazide at 292 m μ which, for the range of concn. examined, follows Beer's law. *Procedure*—Reflux for 2 hr. a mixture of a soln. of 0.3 to 1 mg of the sample with 0.5 ml of semicarbazide acetate reagent (*cf.* Maddigan *et al.*, *Anal. Chem.*, 1951, **23**, 1691). Make up the cooled soln. to 100 ml with absolute ethanol, measure the absorption at 292 m μ , and compare with results obtained similarly with known amounts of pure I or II. To extract I or II from tablets,

shake one-half to two powdered tablets with warm absolute ethanol for 20 to 30 min., make up the cooled soln. to 50 ml, and filter. Use 5 ml of the filtrate for the determination as previously directed.

P. S. ARUP

1964. Chromatographic separation and analysis of naphazoline and its hydrolytic degradation products. M. A. Schwartz, R. Kuramoto and L. Malspeis (Columbia Univ. Coll. of Pharm., New York, N.Y.). *J. Amer. Pharm. Ass., Sci. Ed.*, 1956, **45** (12), 814-817.—Naphazoline (I) is hydrolysed in hot neutral or alkaline soln. to N-(1-naphthylacetyl)ethylenediamine (II), 1-naphthylacetic acid (III) and ethylenediamine. A method is described for the partition chromatographic separation and spectrophotometric determination of I, II and III with a precision of $\pm 3\%$. *Procedure*—Add the sample soln. (2 ml) to a chromatographic column of silica gel (15 g) containing H_2O (15 ml) as stationary phase, elute III with $CHCl_3$ (100 ml) and measure the extinction at 283 m μ . $E_{1\%}^{1\text{cm}}$ (283 m μ) for III = 360. Add a fresh sample soln. (2 ml) to a column of Celite 545 (20 g) containing borate buffer (pH 8.5) (15 ml) as stationary phase and pass *n*-heptane- $CHCl_3$ (65:35) through the column. Reject the first 70 ml of eluate, collect the next 125 ml (containing I) and measure the extinction at 282 m μ . $E_{1\%}^{1\text{cm}}$ (282 m μ) for I = 340. Change the eluent to 100% $CHCl_3$. Reject the first 10 ml of eluate, collect the next 100 ml (containing II) and measure the extinction at 284 m μ . $E_{1\%}^{1\text{cm}}$ (284 m μ) for II = 314.

A. R. ROGERS

1965. Conductimetric determination of sulphonamides in non-aqueous solutions with aqueous reagents. C. G. Macarorici (University "V. Babeş," Cluj, Romania). *Rev. Chim., Bucarest*, 1956, **7** (1), 79-92.—Conditions were investigated for the conductimetric titration of sulphonamides, dissolved in ethanol or acetone, with aq. NaOH, HIO_3 and $AgNO_3$. Satisfactory results (error $< 2\%$) are obtained with NaOH and HIO_3 by measuring the titre between two discontinuities in the conductivity curve; with $AgNO_3$ it is necessary to add approx. the correct amount of NaOH first. Equally satisfactory results are obtained by titration with aq. $AgNO_3$, with diphenylcarbazone or the sodium salt of eosin as adsorption indicator.

A. B. DENSHAM

1966. Use of two standards in the quantitative evaluation of chromatograms [of sulphonamides] after elution. I. Jakubec and M. Zahradníček (Inst. Pharm. Chem., Pharm. Fac., Brno, Czechoslovakia). *Chem. Listy*, 1956, **50** (9), 1459-1465.—A new (two standard) method for the chromatographic determination of sulphonamides gives results that are more accurate than those obtained by the one-standard method, and that are independent of the ratio of concn. of sample to standard.

J. ZÝKA

1967. Barbiturates. Investigation and determination in pharmaceutical preparations. I, II. C. Stainier, C. Lapière and S. de Tiège-Robinet (Inst. Pharm., Univ. Liège, Belgium). *Ann. Pharm. Franç.*, 1956, **14** (5), 384-398; (6), 476-492.—Various methods of detection, identification and determination are reviewed, including alkalimetry in aq. and non-aq. solvents by using indicators or potentiometry, argentimetry and mercurimetry, colorimetry and u.v. absorption spectrometry.

Bromimetry for unsaturated radicals and determination of halogen content can be used for appropriately substituted barbiturates. The separation, particularly by solvent extraction, of barbiturates from possible accompanying compounds in pharmaceutical preparations is reviewed and described for several examples. (53 references.)

E. J. H. BIRCH

See also Abstracts 1889, 1922, 1923.

Food

1968. Estimation of total creatinine content in food. D. Pfeil (Chem. Untersuch., Saarland, Saarbrücken). *Z. anal. Chem.*, 1957, **154** (1), 5-7.—Creatinine may be isolated on a paper chromatogram and observed by irradiation with a mercury-vapour lamp. As little as 3 to 5 μg of creatinine may be detected in this way.

M. F. C. LADD

1969. A new colorimetric method for the estimation of reducing sugars. II. J. K. Roy (West Bengal Public Health Lab., Calcutta). *J. Indian Chem. Soc., Ind. Ed.*, 1956, **19** (2), 83-86.—The colorimetric method of Mitra and Roy (*Anal. Abstr.*, 1956, **3**, 241) is successfully used for the estimation of sucrose in commercial cane sugar, sucrose and invert sugar in molasses, and starch in different foodstuffs such as rice, atta, flour, barley and potato.

I. JONES

1970. Simultaneous moisture determinations in a number of samples of starch. M. Ulmann and F. Schierbaum (Inst. für Ernährungsforschung, Potsdam-Rehbrücke, Germany). *Stärke*, 1956, **8**, 81-87.—A method is described for drying samples of starch by exposure to i.r. radiation on a revolving turn-table in a drying oven. The maximum time required for effective drying is 30 min. compared with 4 hr. by the usual method of heating in a drying oven at 120°.

P. HAAS

1971. Glutamic acid decarboxylase in cereals. I. Paper-chromatographic detection of the formation of γ -aminobutyric acid. M. Röhrlich and R. Rasmus (Versuchsanstalt für Getreideverwertung, Berlin). *Z. Lebensmittelforsch.*, 1956, **104** (5), 313-316.—A method is described for the detection and quant. determination of γ -aminobutyric acid in aq. extracts of crushed wheat germ, by means of a circular chromatogram with isopropyl alcohol-glacial acetic acid-water (25:6:5) as solvent mixture, and development with ninhydrin. The amount of γ -aminobutyric acid formed by the decarboxylation of glutamic acid was found to be approx. 2.6 mg per gram of wheat germ.

S.C.I. ABSTR.

1972. Characterisation by paper electrophoresis of milk proteins and their conversion products. R. Schober and H. Hetzel (Staat. Milchwirtschaft. Lehr- und Forschungs., Wangen im Allgäu, Germany). *Z. Lebensmittelforsch.*, 1956, **104** (5), 323-327.—Examination by paper electrophoresis of sterile milk casein showed no changes in solubility, phosphorus content or electrical behaviour, as compared with native casein. The apparatus of Turba and Enekel (*Naturwissenschaften*, 1950, **37**, 93) was used and the paper was developed with Azocarmine B. In contrast, high-temp. treatment results in essential changes in the protein composition of milk serum. With various kinds of cheese

the first whey (broken whey) was compared with that collected after 5 hr.; the observed changes of the percentage constituents of separate protein components are discussed. In Limburg cheese ripening, no change in phosphorus content of the separate casein components was found. The sources of error in the dyeing of casein with Azocarmine B are discussed. S.C.I. ABSTR.

1973. Determination of methanol in official fruit juices and in several preparations with a vegetable-juice base. G. le Moan (Lab. de Toxicologie, Fac. de Pharm., Paris, France). *Ann. Pharm. Franç.*, 1956, **14** (6), 470-475.—Of the several methods examined, most suffered interference from ethanol or were too insensitive. The method in which Schiff reagent was used, rendered specific for formaldehyde by the Denig's method, the optimum conditions for which were investigated by Jacquin and Tavernier (*Ann. Tech. Agric.*, 1953, **2**, 113), is satisfactory. *Procedure*—The fruit juice or distilled spirit (60 ml) is mixed with 60 ml of water and 2 ml of 0.1 N NaOH, and distilled; the 60 ml of distillate is redistilled to give 25 ml of final distillate. The method of Jacquin and Tavernier (described) is then applied to determine the methanol. The methanol is determined in several fruit juices, syrups, cider and spirits distilled from cider. E. J. H. BIRCH

1974. Microscopical detection of apple pulp in preserved fruits and jams. H. Ludwig (Chem. Untersuch., Freiburg i. Br., Germany). *Z. Lebensmittl. Untersuch.*, 1956, **104** (5), 327-335.—The starch and fibre contents of various kinds of commercial apple sauces and apple pulp used in jam manufacture were studied; samples of 50 g were used. To identify starch-free apple pulp and also to distinguish between that and other added fruit pulps, a double staining method with methylene blue (0.01% soln.) and ruthenium red (0.06% soln.) was satisfactory in most cases for differentiation, and for the detection of small amounts of apple pulp. The shape of the fruit cells must also be considered. The method is not quant., but the behaviour of many separate kinds of fruit pulp with the dye mixture is described. S.C.I. ABSTR.

1975. Non-specific detection of preservatives in jams with osmophile yeasts. M. J. Bernaerts (Lab. Central, Min. des Affaires Economiques, Brussels, Belgium). *Z. Lebensmittl. Untersuch.*, 1956, **104** (6), 405-412.—The simple technique described is based on the measurable vol. of CO₂ produced from a sample of jam (10 g) inoculated with a suspension of young yeast cells (*Saccharomyces rouxii*) (0.1 ml), of known cell count. Various factors that influence the result are discussed, e.g., the pH of the sample and the retardation of CO₂ formation in overboiled jam. Complete absence of gas formation indicates the presence of preservatives. Gas production less than 50% of a given min. value, but above zero, indicates small quantities of preservatives. S.C.I. ABSTR.

1976. Specific detection of bromoacetic acid and its derivatives. K. Woidich, L. Schmid and H. Gnauer (Lebensmittelversuchsanstalt, Wien). *Z. Lebensmittl. Untersuch.*, 1956, **104** (6), 401-405.—The method described for the detection of bromoacetic acid as its ester in foods is based on extraction with ether and saponification, followed by ascending

chromatography with cyclohexane-dioxan-glacial acetic acid-water (10:8:4:4) for 2 to 3 hr. After treatment with aq. NH₃ and drying, the chromatogram is sprayed with phenol red and chloramine T, and the bromoacetic acid is identified as a blue spot on a yellow ground. The method is sensitive to 0.4 mg per litre or per kg. S.C.I. ABSTR.

1977. A simple test for the detection of date- and tamarind-seed adulterants in coffee. C. P. Natarajan and D. S. Bhatia (Div. of Food Processing, C.F.T.R.I., Mysore). *Bull. C.F.T.R.I., Mysore*, 1956, **5** (11), 262-263.—Extract 1 to 2 g of coffee with 200 ml of H₂O for 5 min., and dry the residue. Sprinkle the dry powder on a filter-paper, and drop on aq. NaOH (2%). After 5 to 10 min., a yellow colour diffuses from the coffee particles, a pink colour from the tamarind seed, and a red colour from the date seed. Amounts >10% can be easily detected and down to 5% can be detected after some experience. G. THACKRAY

1978. Refractometric analysis of beer. Development of calculated formulae for alcohol and actual extract from the refractive index and specific gravity of beer. E. Schild and G. Irrgang (Inst. für chem.-tech. Analyse Weihenstephan, Germany). *Brau-wissenschaft*, 1956, **9** (12), 314-323.—The literature from 1843 is discussed. Accurate analyses of the last ten years indicate that present-day beer values cannot be satisfactorily determined by former calculated formulae, probably because raw materials have changed, e.g., barleys with poorer protein are used and the fermentation grade of modern beer is higher. The relations between specific gravity and refractive index of samples of beer and values of the original wort have been studied and new formulae developed. These values were in good agreement with results of distillation analyses and were greatly superior to those of the old refraction processes. A mathematical discussion is presented. S.C.I. ABSTR.

1979. Comparative studies of methods of hop analysis. II. Estimation of humulone and other resin constituents. L. R. Bishop. *Brasserie*, 1956, **11**, 255-274.—*Cf. Anal. Abstr.*, 1956, **3**, 1520. S.C.I. ABSTR.

1980. Chemical test for screw stoppers [used in the brewing and mineral-water industries]. K. W. Allen (Northampton Poly., St. John Street, London). *J. Inst. Brew.*, 1956, **62** (4), 337-338.—Ebonite screw stoppers used in the brewing and mineral-water industry sometimes cause tainting owing to a high content of S. The following method of analysis for sulphide S may be used. Boil a whole stopper rapidly in 5% (w/v) citric acid soln. (150 ml) for 10 min., collecting the distillate (100 ml) in two equal portions in Nessler cylinders containing 4% (w/v) NaOH (40 ml). Treat each with glacial acetic acid (5 ml), 1% gum arabic (2 ml) and saturated Pb acetate (2 ml). Compare the colour visually with standards made from water containing gum arabic soln. (2 ml), saturated sodium sulphide soln. and a measured quantity of standard Pb acetate soln. A comparison of results obtained with stoppers from various sources shows that a mean total of 15 µg of sulphide S is satisfactory, and that an H₂SO₄ wash on removal of the stopper from the mould reduces the sulphide content below this level. D. G. LLOYD

1981. Routine determination of phosphoric acid in wine-ash. J. Schneyder (Landwirtsch.-Chem. Bundesversuchsanstalt, Vienna). *Mitt. Wein- u. Obstbau, Wien, A*, 1956, **6** (6), 309-313.—The method of Rancke-Madsen and Kjaergård (*Anal. Abstr.*, 1954, **1**, 60) is adapted for the titration of soln. of wine-ash by the preliminary removal of Fe^{3+} and Al^{3+} by treatment with a cation exchanger. The mixed indicator used in the determination of the increase in $[\text{H}^+]$ caused by the addition of a slight excess of CeCl_3 is modified to contain methyl orange, bromocresol green and methyl red ($1 + 5 + 1$). The results obtained agree well with those determined by a standard method. *Procedure*—A soln. in dil. acid of the ash from 25 or 50 ml of wine is boiled for a short time with 0.5 or 0.3 g of Amberlite IR-120 or Dowex 50, filtered, and titrated to a pure grey end-point with 0.1 N KOH in the presence of the mixed indicator. After the addition of 2 to 4 drops of 80% (w/v) aq. CeCl_3 , a second titration to the same end-point gives a measure of the H_3PO_4 . P. S. ARUP

1982. Spectrophotometry in analysis of oils and fats. N. H. E. Ahlers (Unicam Instruments Ltd., Cambridge). *Paint Tech.*, 1956, **20**, 237-241.—The applications of u.v., visible and i.r. absorption spectroscopy, Raman spectroscopy and flame photometry as modern analytical techniques are described. Descriptions of modern instruments are included. D. R. DUNCAN

1983. Volumetric determination of water by the Karl Fischer titration. III. Determination of water in fatty oils and fats. V. Gauno-Jensen (Danish Pharm. Coll., Copenhagen). *Dansk Tidsskr. Farm.*, 1956, *Suppl. 2, Festskr. Svend Aage Schou*, 133-149.—Small amounts of water in fatty oils and fats can be accurately determined by the Karl Fischer procedure with the use of an excess of the reagent, and back-titration after 10 min. No evidence is found of side-reactions. Results obtained by the acetyl chloride method of Smith and Bryant are high, but are comparable with the Karl Fischer results, provided that the time of standing of the mixture of the sample with the reagent is reduced to a minimum. P. S. ARUP

1984. Iodimetric processes for determination of peroxide number in edible oils. H. Hadorn, K. W. Biefer and H. Suter (Lab. V.S.K., Basel, Switzerland). *Z. Lebensmittelforsch.*, 1956, **104** (5), 316-323.—The method of Hadorn and Jungkunz (*Anal. Abstr.*, 1954, **1**, 1684) was re-examined and compared with Sully's method (*Analyst*, 1954, **79**, 86) and Wheeler's method (*Oil and Soap*, 1932, **9**, 89). With the usual commercial oils with a peroxide no. of ≈ 20 , the results from all methods were in good agreement. With oils with very high peroxide no., the method of Hadorn and Jungkunz gave low results. The size of the granules, rather than the quantity of KI used, affected the results. When the finest powdered KI was used, the true values were obtained almost without exception, and also when the quantity of KI was reduced from 1.0 to 0.1 g. The modified method of Wheeler is recommended; small quantities of reagents are used, at room temp., and reproducible results in good agreement with those of other methods are obtained. S.C.I. ABSTR.

1985. Determination of oil acidity from oil seeds. G. Bigoni (Soc. Gaslini, Genoa, Italy). *Olii Min.*, 1956, **33** (9), 306-308.—To prevent alteration of oil

during solvent extraction, a method of extraction is suggested in which the seeds are ground in the presence of solvent (light petroleum) and the oil soln. is titrated directly. Treatment at 100° to 105° of the unbroken seed is used to block the lipases. The results obtained, with some exceptions, agree with or are lower than those obtained by conventional methods. Some typical results for different seed oils under various conditions are tabulated. C. A. FINCH

1986. Identification of rape oil in olive oil. J. Vizern (Vizern and Guillot Anal. Lab., Marseilles). *Olii Min.*, 1956, **33** (10), 345-347.—A specific reaction for detecting rape oil in the presence of arachis oil (*cf. Compt. Rend.*, 1953, **236**, 813) has been extended to olive oil. The reaction is based on fractional crystallisations of potassium soaps in acetone at different temp. Under fixed conditions, the presence of 5% or more of rape oil is shown by a characteristic milkiness. C. A. FINCH

1987. Development of a simple method for the fractionation and analysis of mono- and di-glyceride mixtures. O. S. Privett (The Hormel Inst., Univ. of Minnesota, U.S.A.). *Hormel Inst., Ann. Rep.*, 1955-56, **13-20**.—The micromolecular distillation technique described in the *Hormel Inst., Ann. Rep.*, 1954-55, for estimating the mono-, di- and tri-glyceride contents of commercial emulsifiers can be applied to the analytical determination of these compounds with little error (possibly 2 to 3%) due to disproportionation. This technique is very sensitive to impurities formed during the synthesis of monoglycerides by the acetone-glycerol procedure. S. C. JOLLY

1988. Separation of neovitamin A₁ from all-trans vitamin A₁ by chromatography on alumina. B. Barnholdt (Nat. Vitamin Lab., Copenhagen, Denmark). *Nature*, 1956, **178**, 1401-1402.—The two vitamin-A₁ isomers in samples of fish-liver oil or synthetic vitamin can be separated by fractional chromatography of ≈ 1.5 mg of a mixture of the alcohols of the two vitamins on a column (75 cm \times 0.9 cm) of Al_2O_3 , prepared (as described) from finely ground $\text{Al}(\text{OH})_3$. Mixtures of diethyl ether and light petroleum with increasing contents (2 to 25% v/v) of the ether are used for the elution; the flow rate is ≈ 1.3 ml per min. at a pressure of 0.4 to 0.5 atm., and the eluate is collected in 4-ml fractions. The loss of vitamin is from 8 to 10%. By measuring the extinction, at 325 m μ , of the separate fractions the ratio of the two isomers can be calculated. This procedure gives a more effective separation than is obtained by chromatography on activated dicalcium phosphate or coarse-grain Al_2O_3 . W. J. BAKER

See also Abstracts 1889, 1901, 1929, 2036, 2039.

Sanitation

1989. Spectrometric investigations of atmospheric pollution. R. A. Friedel (Central Expt. Sta., Bureau of Mines, Bruceton, Pa., U.S.A.). *Anal. Chem.*, 1956, **28** (12), 1806-1810.—Applications of spectrometry to the study of atmospheric pollution are reviewed briefly. They include the use of mass spectrometry for determining NO_x and other components in complex mixtures, and the use of i.r. methods for measuring specific hydrocarbons in

coal-mine gases, etc. The presence of nitro and possibly other nitrogen-oxygen groups in a sample of air has been demonstrated by a combination of methods. Suggestions are made for new approaches to this study. K. A. PROCTOR

1990. Automatic apparatus for determination of nitric oxide and nitrogen dioxide in the atmosphere. M. D. Thomas, J. A. MacLeod, R. C. Robbins, R. C. Goettelman, R. W. Eldridge and L. H. Rogers (Stanford Res. Inst., Menlo Park, Calif., U.S.A.). *Anal. Chem.*, 1956, **28** (12) 1810-1816.—An automatic sampling and recording apparatus for the continuous determination of NO and NO₂ in the atmosphere is described. Two special absorbers are used for the absorption of NO₂ in a modified Griess reagent, followed by colorimetric recording. One absorber measures the NO₂ alone, the other measures NO₂ plus NO after the NO has been oxidised. The standard error is about $\pm 5\%$. The instrument is calibrated empirically with known mixtures of the oxides with air, and the concn. limits range up to about 1 p.p.m., but this can be extended or reduced. The interference effects of a number of organic compounds have been studied and the results are listed. K. A. PROCTOR

1991. Conductimetric titrations in chelatometry. II. Determination of total hardness of water. F. Vydra and M. Karlik (Vysoká škola chem. technol., Prague, Czechoslovakia). *Chem. Listy*, 1956, **50** (11), 1754-1756.—By using a conductimetric indication of the equivalence point, the total hardness of water may be determined compleximetrically. *Procedure*—Dilute the sample (containing ≥ 4 mg of Ca plus Mg) to 200 ml, add 0.05 M Na₂B₄O₇ (5 ml), KCN soln. (10%) (0.3 ml) and triethanolamine (10%) (0.3 ml), and titrate with 0.02 M EDTA, measuring the conductivity after each addition of the titrant (0.2 to 1 ml). Copper, Fe and Al are masked with KCN and triethanolamine; Mn must be absent. The determination can be carried out even when Eriochrome black T cannot be used as indicator, e.g., in the presence of ClO⁻. J. ZYKA

1992. Polarographic testing of drinking and usable water. I. Determination of hardness and alkali-metal content. J. Prosz and K. Györfi (Dept. Inorg. Chem., Technol. Univ., Budapest). *Chem. Anal., Warsaw*, 1956, **1** (2-3), 21-28.—Polarographic methods, with mercury-jet electrodes, for the direct determination of K, Na, Ca and Mg are described. Magnesium is determined with 0.4 to 0.8 M tetramethylammonium chloride at pH 5.4 to 6.8 as the base electrolyte. The diffusion current is proportional to the concn. of Mg in the range 5×10^{-4} to 3×10^{-3} M. Calcium is determined similarly at concn. of 2×10^{-4} to 5×10^{-3} M in the pH range 4.8 to 9.4. Potassium and sodium are determined as their sum at any pH value above 4.5. The half-wave potentials are -2.15 V for K, -2.16 V for Na, -2.36 V for Ca and -2.53 V for Mg. Results with pipe-water, river, well and mineral waters were in good agreement with those obtained by compleximetric methods for Ca and Mg and an ion-exchange method for Na and K. K. F. SPOREK

1993. Specific colorimetric method for determination of traces of chlorine in chlorinated tap water. L. M. Kul'berg and L. D. Borzova (Saratov Univ., USSR). *Ukrain. Khim. Zhur.*, 1956, **22** (1), 100-105.—To 100 ml of water, containing $> 1 \mu\text{g}$ of

Cl per ml, are added 1 g of NaOH, 1.5 ml of aniline and 3 g of phenol, and the extinction is measured after 20 min., at 610 m μ . For lower contents of Cl, 200 ml of water is extracted with 30 ml of CHCl₃; after addition of a few drops of 5 N HCl, the extract is shaken for 1 min. with 3 ml of N NaOH, a drop of aniline and 0.1 g of phenol are added to the aq. extract, and the coloration is read as before. The method gives accurate results for concn. of 0.1 to 25 μg of Cl per ml, and is highly specific; other oxidants (Fe²⁺, MnO₂, NO₂⁻, chloramines and chloramines) do not interfere. R. TRUSCOE

1994. Determination of nitrate in fresh water. Concentration of samples by an ion-exchange procedure. A. D. Westland and R. R. Langford (Opeongo Limnol. Lab., Dept. Lands and Forests, Whitney, Ont., Canada). *Anal. Chem.*, 1956, **28** (12), 1996-1998.—The method described extends the lower limit of determination of NO₃⁻ in fresh-water samples to ≈ 0.06 p.p.m. *Procedure*—Adjust the pH value of the sample (500 ml) to between 5 and 7 (with 0.01 N acetic acid or NaHCO₃) and raise the concn. of Cl⁻ to 0.001 M. Pass the water through a column (8 cm \times 0.8 cm) of Amberlite IR-4B at the rate of 1 to 1.5 ml per min. and then remove the NO₃⁻ by elution with 1% NaCl soln., making the eluate up to 50 ml. To a 5-ml aliquot add exactly 0.4 ml of 0.6% (w/v) sulphuric acid soln. (to sequester NO₃⁻) followed, after 10 min., by 5.4 ml of 0.001 M soln. of strychnidine in H₂SO₄. Mix, and after ≈ 20 min. measure the extinction in a photo-electric colorimeter with a 6-mm aperture and a 540-m μ filter (the soln. should be protected from bright light). Unless the ion-exchange process of concn. is applied to the sample before the colorimetric procedure, the results can be several hundred per cent. high, owing mainly to hydrolysis of organic N. The calibration curve is constructed from measurements on standard soln. of NO₃⁻ (0.1 to 1 p.p.m.) containing 1% of NaCl. W. J. BAKER

1995. Determination of silver in waters of low mineral content by the method of spectrographic analysis. L. G. Loginova (All-Union Sci. Res. Inst. of Hydrogeology and Engineering Geology). *Zavod. Lab.*, 1956, **22** (11), 1315-1318.—The dried residue of the sample of underground water is mixed with an equal wt. of Li₂CO₃ to act as a temp. stabiliser, and arced in the hollow of a carbon electrode. The line Ag 3280.7 Å is measured. Standards are prepared from a mixture of equal parts of CaSO₄, MgSO₄ and Na₂SO₄ to which are added an equal wt. of Li₂CO₃ and various amounts (0.1 to 0.0004%) of Ag as AgNO₃. G. S. SMITH

1996. Determination of trace amounts of alkylbenzenesulphonates in water. Subcommittee on Analytical Methods. Technical Advisory Committee. Association of American Soap and Glycerine Producers Inc. *Anal. Chem.*, 1956, **28** (12), 1822-1826.—A specific quant. i.r. procedure for the determination of trace concn. of alkylbenzenesulphonates in raw and treated water supplies has been developed. The method involves concn. of the benzenesulphonates by adsorption on activated carbon, desorption, removal of interferences by extraction and hydrolysis techniques, and final quant. determination in the 9.5 to 10- μ region. The entire spectrum from 2 to 15 μ is used qualitatively. Seven laboratories obtained results varying from 0.08 to 0.15 p.p.m. at 9.9 μ and 0.06 to 0.15 p.p.m. at 9.6 μ , on a co-operative sample.

The method is lengthy and would therefore serve best as a referee of proposed shorter methods.

G. P. COOK

1997. Membrane-filter method applied to activated-sludge suspended-solids determinations. R. S. Engelbrecht and R. E. McKinney (Dept. of Sanitary Engng, Mass. Inst. Technol., Cambridge, U.S.A.). *Sewage Ind. Wastes*, 1956, **28**, 1321-1325.—A "Millipore" filter membrane (type HA) of 47 mm diam. was weighed in an aluminium dish (60 mm in diam.) and then transferred to a seamless funnel fastened to a porous plate for supporting the membrane. The sample (25 to 50 ml) was then filtered into a 1-litre filter-flask under reduced pressure. The membrane (with solids) was removed by forceps, replaced in the dish, dried at 103° for 1 hr., cooled and weighed. Detailed results are given which show the precision of this method to be greater than that of standard methods. The standard deviation, with activated-sludge samples containing from 276 to 4746 mg of suspended solids per litre, was generally <1.6%. The method can also be used with samples of raw sewage. S.C.I. ABSTR.

1998. Recent trends in the analysis of industrial wastes. W. A. Moore and M. B. Ettinger (R. A. Taft Sanitary Engng Center, Cincinnati, Ohio, U.S.A.). *Anal. Chem.*, 1956, **28** (12), 1819-1821.—Present trends and probable future needs in the analysis of industrial wastes intended for discharge to surface waters are discussed under the following headings—instrumentation; bio-assay procedures; toxicological examination; development of new criteria of pollution (especially tests for tannins and lignins); adaptation of standard analytical procedures in sewage-disposal and water-treatment practice to the examination of industrial wastes; and the trend towards increasing specificity, e.g., for alkylbenzenesulphonates, and sensitivity, e.g., the C-absorption technique. W. J. BAKER

1999. Spectrophotometric determination of alkylbenzenesulphonate detergents in surface water and sewage. J. D. Fairing and F. R. Short (Monsanto Chemical Co., Dayton, Ohio, U.S.A.). *Anal. Chem.*, 1956, **28** (12), 1827-1834.—The method is based on the isolation of the alkylbenzenesulphonate from interferences, by extraction of its 1-methylheptylamine (I) salt with a I-chloroform soln. and then with a I-hexane soln. after acid hydrolysis of the chloroform extract. The alkylbenzenesulphonate is measured spectrophotometrically by an improved methylene blue procedure. Results from replicate determinations on eight water and sewage samples containing from 40 to 110 µg of alkylbenzenesulphonate had a standard deviation of ±0.3 µg, and were in close agreement with results obtained by an i.r. procedure. G. P. COOK

See also Abstracts 1808, 1817, 1882.

Agriculture and Plant Biochemistry

2000. Radio-strontium fall-out in biological materials in Britain. R. J. Bryant, A. C. Chamberlain, A. Morgan and G. S. Spicer. A.E.R.E. Publication HP/R 2056, 1956, 44 pp.—The development of accurate analytical methods for the determination of ⁹⁰Sr in soils and biological materials, and the results of analyses of soils, hay and grass, sheep bones and milk are reported. These indicate that from the spring of 1955 onwards, the levels of ⁹⁰Sr

in biological materials in the U.K. and the U.S.A. have been similar. The ⁹⁰Sr fall-out derived from megaton weapons is uniform throughout the world, except for local effects due to rainfall variations. Sampling methods and analytical procedures for the determination of ⁹⁰Sr in (a) soil, by HCl extraction, by fusion with NaOH and Na₂CO₃, and by ammonium acetate extraction; (b) animal-bone ash; (c) human-bone ash; (d) dried milk; and (e) vegetable ash, are given in detail. J. M. JACOBS

2001. Rapid direct polarographic determination of zinc in plant-ash solutions. H. L. Barrows, M. Drosdoff and A. H. Gropp (Univ. of Florida, Gainesville, Fla., U.S.A.). *J. Agric. Food Chem.*, 1956, **4** (10), 850-853.—Soln. of plant ash in dilute HCl (containing concn. of Zn of 0.003 to 0.16 mM) can be directly polarographed. An aliquot of the soln. equivalent to 0.01 to 0.12 mg of Zn is mixed with a strongly ammoniacal soln. of KCl, Na₂SO₃ and gelatin and the polarogram is recorded from this soln. There is no interference from Mn²⁺, Ni²⁺, Co²⁺, Cd²⁺, Cr³⁺, Al³⁺ or Fe³⁺ in concn. normally found in plant tissue. N. M. WALLER

2002. A plummet balance for measuring the size distribution of soil particles. T. J. Marshall (Div. of Soils, C.S.I.R.O., Adelaide). *Aust. J. Appl. Sci.*, 1956, **7** (2), 142-147.—In measuring the density of soil suspensions at a predetermined depth and time, the specific-gravity balance described makes use of a glass or plastics plummet. The only adjustment required in use is in the height of the balance; this ensures that the plummet sinks to the correct depth. The percentage of soil in suspension is read on a scale divided into 100 divisions and the balance is sensitive enough (±2 mg) for 1-division accuracy in suspensions containing 20 g per litre. For 50 g of soil per litre, balance sensitivity needs to be ±5 mg. The plummet balance is more accurate than common soil hydrometers at any selected depth, and measurements can be made more rapidly than by the pipette method. B. J. WALBY

2003. An application of a method of gas micro-analysis to the study of soil air. H. R. B. Hack (Cheshunt Exp. Sta., Herts., England). *Soil Science*, 1956, **82**, 217-231.—The need for a method of comparing small and large samples of gas from soil is discussed. For micro-sampling, a hypodermic syringe was inserted into the soil through a transparent plastics sheet 0.5 mm thick which formed a supporting wall for the soil. The method of gas analysis employed was that of Scholander and Evans (*Brit. Abstr. C*, 1947, 253); the accuracy, for 0.35 × 10⁻³-ml samples, was ±0.2 vol.-% when compared with the 0.5-ml analyser of Scholander (*Brit. Abstr. C*, 1947, 94). To obtain macro samples, glass capillary tubes were inserted into the soil to the required depth, glass wool being stuck over the buried end to prevent entry of soil particles; the gas was analysed by the Haldane method. Two principal reasons for the different results of small and large samples are the possibility of drawing the air from large voids when taking large samples and of the glass tube's opening up paths of communication along the tube to other regions of the soil or to the atmosphere above. Considerable differences were found in O and CO₂ of large and small samples extracted from a soil in a glasshouse border; the differences were greatest in artificially compacted top-soil and the reasons for this are discussed. P. HAAS

2004. Determination of readily soluble copper in soil and alluvium: introducing white spirit as a solvent for dithizone. R. H. C. Holman (Geochem. Prospecting Res. Centre, Imp. Coll. Sci. Technol., London). *Bull. Instn Min. Metall.*, 1956, **66**, 7-16.

—Two procedures are described. *Laboratory procedure*—To the sieved sample (0.2 g), passing 80 mesh, are added 5 ml of buffer soln. [ammonium citrate (50 g) and hydroxylamine hydrochloride (20 g) in 1 litre, adjusted to pH 2.0 with HCl, with thymol blue as indicator] and 2 ml of a 0.001% soln. of dithizone in white spirit. The mixture is shaken vigorously for 1 min. and then matched with previously prepared standards. If the colour is above the standard range, measured increments of dithizone are added until a match is obtained. A field procedure is also described. For readily sol. Cu the laboratory procedure has a range of 2 to 270 p.p.m. and an accuracy within $\pm 15\%$; the field procedure has a range of 1.5 to 42 ml of dithizone and an accuracy within $\pm 25\%$. J. M. JACOBS

2005. [Test of normality of] frequency distribution of [an experimental error, with particular reference to] spectrographic error in d.c. arc excitation of soil samples. A. C. Oertel (Div. of Soils, C.S.I.R.O., Adelaide). *Aust. J. Appl. Sci.*, 1956, **7** (2), 133-141.

—The normality of the frequency distribution of an experimental error can always be tested accurately when sufficiently numerous sets of measurements are available and replication in all sets is at least threefold. One derivation of a frequency distribution function for standardised deviates (z) that can be used for this purpose is outlined. Fractions of the total sample of values of z lying in 0.1-unit intervals of the range of z are tabulated corresponding to three- to six-fold replication of measurements, and these are used in testing for the normality specified above. All measurements involved must be essentially of the same nature, although sets of replicates need not have the same mean and standard deviation; nor must the replicates be in any way special measurements for the purposes of the test. The use of the distribution function is illustrated. B. J. WALBY

2006. Colorimetric determination of phosphates in raw materials and fertilisers. K. Lasiewicz and H. Zawadzka (Inst. of Sulphuric Acid and Phosphorus Fertilisers, Lubon, Poland). *Chem. Anal., Warsaw*, 1956, **1** (1), 53-63.—This rapid method, suitable for the works control of raw materials and finished phosphate fertilisers, is based on the formation of molybdenum blue, with metol as reductor. A straight-line calibration curve is given for the range 0.1 to 5 mg of P_2O_5 . Citric acid (0.5 to 5 ml of a 2% soln.) in 100 ml of the final soln. does not affect the results, but >0.6 ml of ammonium citrate soln. (about 50%) and H_2S interfere. The material under test is treated, according to the information required, with either H_2SO_4 - HNO_3 , water, 2% citric acid or ammonium citrate soln. The soln. containing P_2O_5 (5 to 40 ml) is then treated with 10 ml of the reductor soln. (1 g of metol, 5 g of $Na_2SO_3 \cdot 7H_2O$ and 15 g of $Na_2S_2O_5$ in 500 ml of water) and 10 ml of ammonium molybdate soln. (50 g of ammonium molybdate dissolved in hot water, mixed with 500 ml of 10 N H_2SO_4 and diluted with water to 1 litre), and set aside in the dark for 10 min. The mixture is then treated with 20 ml of 2 N Na acetate, diluted with water to exactly 100 ml and the extinction of the soln. is measured, with a 2-cm cell. The results for samples of phosphorus-containing raw materials, superphosphates

and pyrophosphates were in good agreement with those obtained by the conventional gravimetric method. The time required for a determination was about 1 hr. K. F. SPOREK

2007. Chemical aspects of pyrethrum analysis. I. R. G. Barradas. *Chemical Age*, 1956, **76**, 507-510.

—The chemistry of the constituents of pyrethrum flowers, in relation to their assay, is discussed. Three methods of chemical analysis of pyrethrum flowers are reviewed. H. B. HEATH

2008. Colorimetric determination of lindane in soils and crops. E. P. Lichtenstein, S. D. Beck and K. R. Schulz (Dept. of Entomology, Univ. of Wisconsin, Madison, U.S.A.). *J. Agric. Food Chem.*, 1956, **4** (11), 936.—The direct determination of lindane (hexachlorocyclohexane) (**I**) is described. *Procedure*—For soils of low org. content, to ≥ 50 g (according to the expected **I** content) mixed with sufficient **I**-free soil to make 50 g, is added 130 ml of acetic acid, and 30 ml of the acid is distilled off. Zinc (10 g) and malonic acid (20 g) are added to the cooled product, and the determination is completed by the method described by Schechter and Hornstein (*Anal. Chem.*, 1952, **24**, 544). For soils of high org. content, 150 ml of acetic acid and 5 g of malonic acid are added before distilling off 50 ml of the acid. For crops, the fresh plant parts are washed successively with warm water, with acetic acid to remove adherent **I**, and with water. The washed material is diced and mixed in a Waring Blendor, and 40 g is distilled with 130 ml of acetic acid and 5 g of malonic acid until the vol. of acid is reduced to 50 ml; 80 ml of acetic acid is added and the volume is reduced to 100 ml. Zinc and malonic acid are added and the **I** is determined as described above. Nearly 100% of known amounts of **I** added in acetic acid soln. was recovered from all types of sample. S. C. JOLLY

2009. The determination of OO-diethyl O-p-nitrophenyl thiophosphate [parathion] by column chromatography. W. Paulus and H. J. Mallach (Inst. für gerichtl. Medizin, Univ. Bonn, Germany). *Arzneimittel-Forsch.*, 1956, **6** (12), 766-767.—The adsorption of parathion (**I**) on 18 substances was investigated with a variety of solvents. Suitable adsorbents include alumina, active carbon, Florisil and silica gel. **I** is most strongly adsorbed from benzene or light petroleum soln. and most readily eluted by ether or $CHCl_3$. Column chromatography is recommended for application in the purification and analysis of **I**. A. R. ROGERS

See also Abstracts 1864, 1865, 1866, 1959.

5.—GENERAL TECHNIQUE AND LABORATORY APPARATUS

General

2010. Report on recommended specifications for microchemical apparatus. Volumetric glassware. Flasks, pipettes and centrifuge tubes. Committee on Microchem. Apparatus, Div. of Anal. Chem., American Chemical Society (1155 Sixteenth St., Washington, D.C., U.S.A.). *Anal. Chem.*, 1956, **28** (12), 1993-1995.—Standard drawings and measurements are given for calibrated flasks (1 to 5 ml), pipettes (0.2 to 3 ml) for use therewith, and plain and calibrated centrifuge tubes (0.5 to 5 ml) with or without stoppers. W. J. BAKER

2011. **Micro test-tube marker.** S. L. Bonting and G. R. Walters (Coll. of Medicine, State Univ. of Iowa, Iowa City, U.S.A.). *Anal. Chem.*, 1956, **28** (12), 2035-2036.—Details are given of a device for marking micro test-tubes to contain vol. of 20 to 500 μ l. The reproducibility was determined for 20 tubes calibrated to contain 100 μ l. The average vol. was 99.03 μ l, with a standard deviation of 0.72 μ l.
K. A. PROCTOR

2012. **Plastics vessel for pH measurements of small samples.** K. M. Richter (Univ. of Oklahoma School of Medicine, Oklahoma City, U.S.A.). *Anal. Chem.*, 1956, **28** (12), 2036.—Constructional details are given of a plastics vessel for the measurement of the pH of samples as small as 0.25 ml in which the sample chamber closely reflects the size and shape of standard Beckman electrode tips.
K. A. PROCTOR

2013. **Continuous automatic titrator by use of proportional plus integral servo-system.** Shoji Makishima, Yukio Yoneda, Hisashi Morikawa and Kenji Miyao (Dept. of Applied Chem., Faculty of Eng., Tokyo Univ., Hongo, Tokyo). *J. Chem. Soc. Japan, Ind. Chem. Sect.*, 1956, **59** (8), 878-883.—An apparatus for the continuous measurement of a component in aq. soln. was designed with the aid of an automatic control system. The sample flows at a const. rate through a glass container, equipped with a calomel and platinum electrode and a stirrer. The standard soln. is introduced into the vessel through a gear pump (0.6 ml per rev.), its vol. being measured by the revolution of the pump. The p.d. between the electrodes is amplified and the out-put current controls the revolution of the pump; the voltage is approx. proportional to the p.d. The r.p.m. is recorded against time. The titration of Fe^{2+} with 0.05 N KMnO_4 is given as an example. The stability of the system increases with increase in the rate of flow of the sample soln. and with decrease in the concn. of the standard soln. The error is < 1.1% and the deviation is < 0.5%.
K. SAITO

2014. **Micro-titration of organic compounds. V. Fully automatic apparatus for the micro-determination of dissociation constants.** W. Simon and E. Heilbronner (E.T.H., Zurich). *Chimia*, 1956, **10** (11), 256-258.—An automatic apparatus is described for determining the dissociation constants and equiv. wt. of 100 to 500- μ g quantities of organic acids and bases in water or organic solvents. It is necessary to weigh the samples, but the apparatus then first checks a glass electrode against a calomel electrode, with a standard buffer, and then carries out a pH titration which is recorded. The standard error for a single measurement is ± 0.06 in pK and $\pm 4.9\%$ for equiv. wt., but can be improved to ± 0.02 in pK and $\pm 1.4\%$ in equiv. wt. by carrying out 12 separate measurements. Thirty measurements can be done in a day.
A. B. DENSHAM

2015. **Liquid-liquid continuous extractor for solvents heavier than water.** C. E. Pierce and R. E. Peterson (Nat. Inst. Health, Bethesda, Md., U.S.A.). *Anal. Chem.*, 1956, **28** (12), 2029-2030.—The extractor assembly described gives a rapid rate of extraction because, through the action of a rotating glass ball, a large surface-film of fresh aq. phase is continuously exposed to solvent and there is continuous mixing. Because the system is air-tight there is little tendency to emulsion formation.

Operational efficiency is shown by curves for the removal of steroids from 1 to 3 litres of water, e.g., hydrocortisone can be extracted with dichloromethane from one litre of H_2O at a rate such that one-half of the steroid is extracted in 18 min. as compared with 84 min. in the Hershberg-Wolfe extractor. From 0.2 to 4 litres of urine can also be extracted rapidly with a small vol. of solvent.
W. J. BAKER

2016. **Burette pump for handling two-phase liquids in quantitative analysis.** W. R. Dunnivant (Aero. Res. Lab., Wright-Patterson Air Force Base, Ohio, U.S.A.). *Anal. Chem.*, 1956, **28** (12), 2034-2035.—The device described is a rapid and accurate means of titrating an unstable soln. or liquid which has been prepared or stored under a protective liquid. It allows the sample to be withdrawn from the main bulk of the soln. still protected by the second liquid phase. The apparatus is useful in the standardisation of CrCl_2 soln., a known vol. of which can be run under the surface of an excess of a soln. of $\text{Fe}_2(\text{SO}_4)_3 \cdot (\text{NH}_4)_2\text{SO}_4$, which is then back-titrated with $\text{K}_2\text{Cr}_2\text{O}_7$ soln. With a 50-ml burette and dodecane as the protective layer an accuracy > 99.7% is attainable.
W. J. BAKER

2017. **Calculation of transfers needed in counter-current distribution.** E. Nelson (Univ. of California Medical Center, San Francisco, U.S.A.). *Anal. Chem.*, 1956, **28** (12), 1998-2000.—A method is described for calculating the no. of transfers needed to effect a given degree of separation between a pair of solutes distributed in the countercurrent process. Applications of the equations developed are illustrated, and possible sources of error in the method are indicated.
K. A. PROCTOR

2018. **Simple apparatus for the change-over from reflux to distillation.** H. F. Bauer (Prairie Regional Lab., Nat. Res. Council, Saskatoon, Saskatchewan, Canada). *Canad. J. Technol.*, 1956, **34**, 397-398.—An attachment, embodying a T-shaped three-way stopcock, enables a change from boiling under reflux to distillation to be made merely by turning the stopcock.
S.C.I. ABSTR.

2019. **Cellulose acetate in chromatography.** G. M. Gray (Lister Inst. of Preventive Medicine, London). *Chem. & Ind.*, 1957, (1), 18.—A secondary cellulose acetate, acetyl value 52.5% as acetic acid, is an excellent support in a partition system with purely organic solvents. Suitable solvents for the stationary phase and others for the mobile phase are listed.
O. M. WHITTON

2020. **Chromato-polarographic studies. X. Testing and preparation of rubber adsorbents for reversed-phase partition chromatography.** W. Kemula and K. Butkiewicz (Dept. of Inorg. Chem., Univ., Warsaw). *Chem. Anal., Warsaw*, 1956, **1** (2-3), 56-60.—Powdered rubber is considered to be the most satisfactory adsorbent for partition chromatography, but it should comply with the following requirements—it should undergo swelling with many solvents but not dissolve in them, be easy to divide into small grains, be stable to acid and alkaline media and not absorb the tested substances. Rubber with optimum properties was obtained by vulcanising at 151° for 50 min. a mixture of natural rubber, sulphur and tetramethylthiuram disulphide (200:24:4).
K. F. SPOREK

2021. **Ultra-violet scanner-camera for paper chromatography.** N. A. Drake, W. J. Haines, R. E. Knauff and E. D. Nielson (Upjohn Co., Kalamazoo, Mich., U.S.A.). *Anal. Chem.*, 1956, **28** (12), 2036-2038.—Constructional and operating details are given of a scanner-camera which has been used extensively for the visual and photographic detection of u.v.-absorbing steroids and other materials on paper chromatograms. K. A. PROCTOR

2022. **A radiological detector for gas chromatography.** C. H. Deal, J. W. Otvos, V. N. Smith and P. S. Zucco (Shell Development Co., Emeryville, Calif., U.S.A.). *Anal. Chem.*, 1956, **28** (12), 1958-1964.—The detector comprises a special ionisation chamber with self-contained radioactive source, an electrometer amplifier with built-in compensating voltage supply, a potentiometer-type strip chart recorder, and an electronic temp. controller for the ionisation chamber. The detector is insensitive to gas flow rate and has a rapid response and high stability. Under standard conditions of operation, a concn. of 0.01 mole-% of heptane in nitrogen produces a signal-to-noise ratio of 2 to 1 and would thus be detectable. The radioactive source is ^{90}Sr - ^{90}Y , which is a pure β -emitter and has a relatively long half-life of approx. 19 yr. K. A. PROCTOR

2023. **Tray for dipping chromatograms.** N. J. Morris and A. C. F. Mason (U.S. Dept. of Agric., New Orleans, La., U.S.A.). *Anal. Chem.*, 1956, **28** (12), 2038.—The tray described is made from borosilicate glass tubing and is intended for applying reagents to developed chromatograms by uniform immersion in about 50 ml of reagent. The tray ensures positive and uniform wetting of papers up to 22.5 in. in width, and is easy to clean, inert to corrosive reagents and free from sources of contamination. K. A. PROCTOR

2024. **A modified Stormer viscometer for absolute viscosity measurements.** E. R. Ballantyne (C.S.I.R.O., Div. Bldg Res., Melbourne). *Aust. J. Instrum. Tech.*, 1954, **10**, 102-113.—A modified Stormer viscometer with two closed cylindrical rotors of the same diameter but different heights, and a cylindrical cup without baffles, is described. The theory of the modified instrument for both Newtonian and non-Newtonian liquids is given and its method of use outlined. Experiments showed that the viscosity of Newtonian oils, if greater than two poises, could be measured to an accuracy within $\pm 2.5\%$ by calculation from the dimensions of the instrument. Some unexplained variations in the end effect showed that more reliable results were obtained by using the two rotors and calculating the viscosity from the dimensions of the instrument than by using a single rotor and calibrating with oil of known viscosity. CHEM. ABSTR.

Optical

2025. **A double-beam microspectrometer.** G. H. Haggis (Middlesex Hospital Medical School, London). *J. Sci. Instrum.*, 1956, **33** (12), 491-493.—A modified single-beam spectrometer, fitted with a small rocking mirror to provide a double beam through a reflecting microscope, is described. The ratio of the intensities of the two beams is determined electronically, and automatically recorded. G. SKIRROW

2026. **Choice of apparatus in emission spectrographic analysis.** A. Hulanicki (Dept. of Inorg. Chem., Univ., Warsaw). *Chem. Anal., Warsaw*, 1956, **1** (1), 21-33.—A survey of instruments and techniques used in emission spectrographic work is presented and details are given of the optimum conditions applicable in specific cases. The method used for registration of lines and for the measurement of their intensity is one of the main factors affecting the precision of results. Visual analysis, which is simple and rapid, is suitable when an error of 20% can be tolerated. By photographic registration the error may be reduced to 5%. Photoelectric methods usually give results with a precision of 1% or better. K. F. SPOREK

2027. **Direct-reading analysis with the medium quartz spectrograph.** D. J. Webb (Hilger & Watts Ltd., London). *Hilger J.*, 1955, **2** (2), 19-24.—The Hilger direct-reading attachment described is designed to solve problems where the average dispersion of the medium quartz spectrograph (1 m μ per mm at 200 to 340 m μ) is adequate and no more than ten elements have to be determined. The illustrated discharge stand is of a new design, incorporating horizontal discharge, which may be used with any of the three discharge generators described. Having 11 photomultipliers, the attachment provides for an internal standard line which is made use of in the manual method of temp. compensation. The electronic console illustrated, available either as a bench or a desk, provides the high potential supply for the photomultipliers, controls the duration of the exposure, and measures and presents the results of the analysis. Potentials proportional to discharge are built up in plastics film-type condensers and can be stored or read and re-read on a meter or a pen-recorder. The standard deviation of a measurement averages about $\pm 2\%$ of the content for all elements with a concn. above 0.01%. The limit of detection, arbitrarily defined, is about 0.003%. E. G. CUMMINS

2028. **Design for voltage generation in spectrochemical analysis, with switching device.** K. Möhl, E. Schael and J. Bruch. *Arch. Eisenhüttenw.*, 1955, **26**, 669-673.—Investigations into the effect of primary voltage in spectrochemical analysis show that the height of the primary voltage of the Feussner spark generator affects spectral line intensity, and intensity differences, in a manner analogous to that of condenser capacitance. With falling voltage, spectral line intensity decreases, the intensity reduction for ionic lines being the most marked. Voltage fluctuations are therefore a source of error in quantitative spectrochemical analysis because they disturb the intensity relationships of useful line-pairs. In order to avoid voltage fluctuations, an arrangement has been developed which, assuming constancy of electrical supply frequency, generates an equally constant free-running voltage and which operates without automatic control apparatus. It consists of a motor generator set which is synchronised with the supply frequency. The excitation windings are fed from a battery. In addition, the arrangement of a spectrographic switchboard is described, which permits a rapid and faultless changeover from one source of excitation to another, i.e., d.c. arc, intermittent a.c. arc, Feussner spark, etc. D. F. PHILLIPS

2029. **Vacuum ultra-violet spectroscopy.** J. R. Stansfield (Hilger & Watts Ltd., London). *Hilger J.*, 1956, **3** (1), 3-5.—The methods of vacuum u.v.

spectroscopy are summarised from the point of view of instrumentation. Vacuum sparks for emission spectra of metals, and various light sources suitable for absorption measurements are mentioned. Detailed design requirements for the spectrograph itself are listed. The possibilities of several reflectors are discussed and improvements in both photographic and photo-electric detection are reported.

E. G. CUMMINS

2030. An automatic analyser of uranium content in process streams. H. Bisby, L. H. Brown and D. R. Chapman (A.E.R.E., Harwell, England). *J. Sci. Instrum.*, 1956, **33** (12), 467-475.—Contemporary batch samples are taken in cyclic order from process streams (eluate from ion-exchange resins), separately treated with NH_4SCN and analysed by u.v. absorption at 3650 Å. The results are automatically recorded.

G. SKIRROW

2031. Some aspects of infra-red spectrometry in atomic energy. J. Gaunt (A.E.R.E., Harwell, England). *J. Appl. Chem.*, 1956, **6** (7), 277-281.—Applications discussed include the determination of the molecular structure of UF_6 and the isotopic analysis of heavy water.

K. A. PROCTOR

2032. Simple monochromator for the infra-red. R. B. Beevers, G. K. T. Conn and J. Hampson (Physics Dept., The University, Sheffield, England). *J. Opt. Soc. Amer.*, 1956, **46** (11), 997-998.—A simple monochromator is described and illustrated; certain features of the design enable use to be made of relatively inexpensive optical components without introducing undesirable image distortions. The instrument is suitable for the determination of optical constants of samples, but not for precision spectrometry.

B. S. COOPER

2033. Instrumentation for rapid spectrochemical analysis. Optical and X-ray emission monochromators and polychromators. J. W. Kemp (Applied Research Lab., Glendale, Calif., U.S.A.). *Anal. Chem.*, 1956, **28** (12), 1838-1843.—This review of commercially available instruments and their capabilities includes a comparison of optical and X-ray methods, instrumentation, precision and accuracy, sensitivity and speed. (28 references.)

K. A. PROCTOR

2034. Instrumental methods of gamma-ray spectrometry. R. E. Connally (General Electric Co., Richland, Wash., U.S.A.). *Anal. Chem.*, 1956, **28** (12), 1847-1853.—Applications of gamma-ray spectrometry to the rapid analysis of mixtures of gamma-emitting radio-isotopes are discussed. Commercially available pulse-height analysis systems are evaluated, their use in qual. and quant. analysis being considered, and the parameters of importance in the selection of the sensing unit are reviewed. The precision to be expected from each type of system is discussed.

K. A. PROCTOR

2035. Simple comparison reflectometer. R. B. Beevers and G. K. T. Conn (Physics Dept., The University, Sheffield, England). *J. Opt. Soc. Amer.*, 1956, **46** (11), 996-997.—An optical arrangement is illustrated which, combined with a monochromator, enables the spectral reflectivity of a sample to be measured rapidly and accurately. Reflectivity is measured at effectively normal incidence.

B. S. COOPER

2036. A modern reflectometer for flour and near-white substances. D. W. Kent-Jones, A. J. Amos, W. Martin and R. A. Scott (The Laboratories, Dudden Hill Lane, Willesden, London). *Chem. & Ind.*, 1956, (50), 1490-1493.—A redesigned optical system has overcome certain difficulties associated with the Series I grader (*Analyst*, 1950, **75**, 127, 133). The Series II grader has a permanent internal standard, a detachable galvanometer system, a separate lamp housing, and a robust cell-holder, and shows a linear reflectivity response. The standardisation of the instrument and the determination of grade value (flour) are discussed. The standard error in the range 0.5 to 3.0 (54 results) is 0.16 grade unit; 12 results in the range 3.0 to 5.5 indicate a similar standard error. The effect of bleaching agents (ClO_2 or ClO_2 plus benzoyl peroxide) is not significant but, after a full bleaching with benzoyl peroxide alone, the flour shows a decrease of 0.2 to 0.3 unit.

G. B. THACKRAY

2037. A new colorimeter. E. Lüscher and J. Durand (Metrohm S.A., Herisau-Lausanne). *Chimia*, 1956, **10** (12), 302.—In the simple colorimeter described, light from a magnetically stabilised source is collimated by a mirror and passes through a heat filter, a glass or interference filter to give the desired colour, a diaphragm, the sample cell, and another diaphragm to a barrier layer photocell. The output from the photocell is fed to a microammeter, with a variable resistance in parallel, so that the scale reading can be adjusted.

A. B. DENSHAM

2038. Recording interferometric arrangement for refractive-index analysis of flowing media. LKB-Produktter Fabriksaktiebolag. Brit. Pat. 760,858; date appl. 7.7.54. Sweden, date appl. 3.9.53.—The apparatus comprises a source of monochromatic light, a collimator, an interferometric beam-splitting device in which two coherent beams of light are obtained by partial reflection and transmission at a half-transparent film, e.g., two 30° - 60° - 90° prisms in which the longer cathetus surface of one prism is equipped with a half-transparent (silver) film in optical contact with the corresponding surface of the other prism, a sample cell with at least two compartments, one adapted for passage of the medium to be recorded and the other filled with a reference medium of approx. the same refractive index, a device for reuniting the two beams of light, a spherical lens system giving two superimposed optical images of the optical middle sections of the two cell compartments perpendicular to the light path, a light-sensitive device in the plane of the images which is moved continuously by a driving arrangement and has, in front of it, a diaphragm with a narrow slit perpendicular to the direction of movement and situated so that it intersects the superimposed images. Preferably, the sample cell contains six compartments so arranged that the optical images of the first and sixth, the second and fifth, and the third and fourth compartments are superimposed, respectively, on the light-sensitive device. The first, third and sixth compartments are coupled in series for passage of the medium to be measured, whilst the remaining compartments are filled with a stationary medium of adjacent refractive index. Three systems of interference fringes are thereby formed on the light-sensitive device: the first is a record of changes in the derivative (with respect to volume) of the refractive index, the second a system of straight fringes usable as reference lines of an

accurate evaluation, and the third is a record of changes in refractive index.

J. M. JACOBS

2039. Photo-electric polarimeter using the Faraday effect. E. J. Gillham (Nat. Phys. Lab., Teddington, England). *Nature*, 1956, **178**, 1412-1413.—In the experimental instrument described, the plane of emergent polarised light is made to oscillate through $\approx 6^\circ$ by utilising the Faraday effect. When the analyser is at 90° to the mean direction of this plane, the intensity of emergent light, although it may be modulated at twice the frequency of oscillation, has a zero alternating component at the fundamental frequency. This condition can be detected by an 11-stage photomultiplier, a.c. amplifier, phase-sensitive rectifier and output meter. The Faraday cell comprises a solid cylinder (10 cm \times 1 cm) of lead-zinc borate glass wound with 18-S.W.G. enamelled copper wire, the coil being supplied with 1 amp. a.c. at 50 c/s (sinusoidal waveform). The stability and performance of the instrument are much superior to those of a visual polarimeter, and its development for use in the sugar industry is being investigated.

W. J. BAKER

2040. Photo-electric apparatus for polarimetric measurements. R. Birebent. *Compt. Rend.*, 1956, **243** (6), 578-580.—It was desired to construct apparatus which would overcome the difficulties encountered from the reduced sensitivity of the eyes when certain parts of the spectrum are observed, or from eyestrain during prolonged observations. This apparatus had to be simple and suitable for mounting on a polarimeter without modification to the latter. A lens and prism optical system was used in conjunction with a diaphragm to throw a real image on a photomultiplier which fed a sensitive meter circuit. A method of selecting each side of a split field in turn was provided by a movable mount for one of the lenses, and if the brightness is equal, no difference in the meter deflection should occur on changing over. The prism was movably mounted so that, if required, the image can be observed through an eyepiece. The halfshade angle had to be rather greater with photo-electric measurement than with visual observation.

J. F. P. H. GREENE

See also Abstracts 1746, 1753.

Thermal

2041. Thermistor-operated temperature control. C. M. Proctor (Dept. of Oceanography, Agric. and Mech. College of Texas, College Station, U.S.A.). *Anal. Chem.*, 1956, **28** (12), 2030-2032.—The regulator permits temp. control to within $\pm 0.01^\circ$ in an uninsulated bath operating 15° above room temp. The desired operating temp. is obtained from a dial setting. No significant drifting was observed during tests, and the temp. could be reset to within 0.02° . Line voltage changes from 100 to 130 V had little effect on the performance of the controller.

K. A. PROCTOR

2042. Liquid bath precision thermostat ranging from about 20° to over 360° . W. M. Smit and H. F. van Wijk (Netherlands Central Inst. for Physico-Chemical Constants, Utrecht, Holland). *Rec. Trav. Chim. Pays-Bas*, 1956, **75** (9-10), 1205-1213 (in English).—A thermostat suitable for the checking of mercury thermometers is described. The bath

liquid is a Na-K mixture. The thermostat can be used from temp. somewhat above room temp. to $>360^\circ$. Its accuracy is $\pm 0.002^\circ$ at 330° , better than $\pm 0.001^\circ$ at low temp. Equilibrium at any desired temp. is attained within 3 hr. M. DAVIS

2043. Cryoscopic determination of purity of highly reactive substances. A. R. Glasgow, jun., and M. Tenenbaum (Nat. Bureau of Standards, Washington, D.C., U.S.A.). *Anal. Chem.*, 1956, **28** (12), 1907-1911.—Constructional details are given of a freezing-point apparatus made of glass and noble metals for determining the purity of reactive substances. Experiments performed on TiCl_4 at different levels of purity are reported.

K. A. PROCTOR

Electrical

2044. Power supply for zone electrophoresis, electro dialysis, and general use. C. M. Proctor (Dept. of Oceanography, Agric. and Mech. College of Texas, College Station, U.S.A.). *Anal. Chem.*, 1956, **28** (12), 2032-2034.—Details are given of a power supply designed to give a constant current output in the range 0 to 30 mA. The unit is built into a steel cabinet, 6 in. \times 9 in. \times 5 in. At 300 V output the ripple was $< 0.01\%$.

K. A. PROCTOR

2045. Multiple determinations with moving-boundary electrophoresis. I. Oreskes and H. Carey (Isaac Albert Res. Inst., Brooklyn, N.Y., U.S.A.). *Clin. Chem.*, 1956, **2** (5), 369-373.—Two dual-analysis cells of the type previously described (*Science*, 1954, **120**, 675) are connected in series so that four expt. can be carried out simultaneously.

H. F. W. KIRKPATRICK

2046. Polarographic analysers. J. V. A. Novák (Polarographic Inst., Czech. Acad. Sci., Prague). *Chem. Anal., Warsaw*, 1956, **1** (2-3), 15-19.—A description is given of automatic analysers based on polarography. Examples are given of instruments suitable for the automatic determination of Ti and Fe in the manufacture of pigments and cyanides, of O in butadiene and ethylene and in boiler water, of Hg in effluents, SO_2 in technical gases and CO in coal mines.

K. F. SPOREK

2047. New methods of polarographic micro-analysis. I. All-purpose plastics vessels for polarographic micro-analysis. Drop-time control in micro-polarographic determinations. Z. Zagórski. *Chem. Anal., Warsaw*, 1956, **1** (2-3), 91-100.—Several micro-cells for polarographic analysis, made of poly(methyl methacrylate), are described. The results showed that as little as 0.05 ml of a soln. could be satisfactorily polarographed. The polarograms were identical with those obtained in 5-cm cells.

K. F. SPOREK

2048. Obtaining derivative curves on a visual polarograph. R. L. Karpovskaya and P. G. Kuznetsov (Central Lab., Siberian Geophysical Trust). *Zavod. Lab.*, 1956, **22** (11), 1284-1286.—Sources of error found during the use of the derivative method described by Aksel'rud *et al.* (*Zavod. Lab.*, 1954, **20**, 6) and suggested improvements are discussed.

G. S. SMITH

2049. The filling of the glass electrode. A. E. Mans (Lab. Phys. Chem., Landbouwhogeschool, Wageningen, Holland). *Chem. Weekbl.*, 1956, **52** (49), 873-882.—Comparatively little is known about a possible shift of the pH scale on modern instruments which occurs whenever the measuring temp. differs from the calibration temp. of the glass electrode (difference = ΔT). The correct pH value of the test soln. differs from that read on the pH scale, in spite of adjusting the temperature potentiometer; the magnitude of this non-adjustable difference (Δ pH) is connected with the pH value of the inner soln. of the glass electrode and with certain other temp. coefficients. In general, mercurous chloride-mercury electrodes with saturated KCl soln., and silver chloride-silver are used as outer and inner reference electrodes, respectively; the pH of the inner soln. is selected over a fairly wide range (pH 1 to 8). Standardisation of the composition of this soln. is desirable. With the above-mentioned arrangement it is shown that a high pH (e.g., pH 7) gives a Δ pH almost three times as great as does a low pH (e.g., pH 1); Δ pH/ ΔT is from 0.01 to 0.03. P. HAAS

2050. Potentiometric pH measurement in strongly alkaline solutions with a new high-alkali glass electrode. G. Gleiche (Hospital Pharm. Lab., Hamburg-Harburg, Germany). *Dtsch. ApothZtg.*, 1956, **96** (45), 1073-1075.—A sensitive highly alkaline glass electrode, suitable for use in pharmaceutical laboratories, is described, which is of low resistance and suitable for direct voltage measurement. The electrode is chemically inert and can be used for conductivity measurements of water and other soln. of low ion content, such as plant extracts. Comparative pH measurements are recorded against standard buffer soln. G. R. WHALLEY

2051. The use of technical propane for removing oxygen from polarographic solutions. O. Kempinski. *Chem. Anal.*, Warsaw, 1956, **1** (2-3), 101-105.—Dissolved O normally interferes with polarographic work owing to its reduction on the mercury electrode with the formation of two waves. The heights of these waves are considerable because of the high solubility of O in water (8 ml of O per litre). Compressed N in steel cylinders is normally employed for removing dissolved O, but an investigation of the suitability of compressed propane, which may sometimes be more readily available, showed that technical propane was a satisfactory substitute for N or CO₂. K. F. SPOREK

2052. A glass-calomel electrode assembly for micro-titration in inert atmospheres. W. Simon (Edwig. Tech. Hochschule, Zurich, Switzerland). *Chimia*, 1956, **10**, 286-287.—A compact glass-calomel electrode assembly for titrations involving 0.3 to 3.0 ml is described and illustrated. E. G. CUMMINS

2053. A simple high-frequency titration apparatus. E. Pungor and K. Huber (Inst. für anorg. und anal. Chem., L. Eötvös Univ., Budapest). *Z. anal. Chem.*, 1957, **154** (1), 1-5.—The simple apparatus described is particularly suited to acid-base titrations. The apparatus works on the principle of

change in circuit Q-factor by change in conductivity of the soln. titrated. A circuit diagram and experimental curves are given. M. F. C. LADD

2054. Amperometry with two platinum electrodes with the cuprous-cupric bromine-bromide system. J. J. Lingane and F. C. Anson (Harvard Univ., Cambridge, Mass., U.S.A.). *Anal. Chem.*, 1956, **28** (12), 1871-1875.—The observed behaviour of the indicator current (i) with two polarised platinum indicator electrodes during coulometric titration with Br⁻ or CuBr₂⁻ in acidic cupric bromide soln. is discussed. The soln. (150 ml) consisted of M NaBr, 0.067 M CuSO₄ and 0.33 M H₂SO₄; the generator electrode area was 5 sq. cm and the constant generating current 12.7 mA. The interpretation of i and the relation between min. i and K (equilibrium constant) for the reaction $2\text{Cu}^{2+} + 7\text{Br}^- = 2\text{CuBr}_2^- + \text{Br}_2$ as given by Farrington *et al.* (*Brit. Abstr. C*, 1953, 374) is inadequate. Correct relations for the system yield an apparent value (K_a) which agrees more closely with the true value calculated from the observed formal potentials. The value of K_a is ≈ 100 times greater than K because the behaviour of the bromine-bromide couple does not comply with the thermodynamic reversibility demanded by the correct treatment. Correct amperometric measurements of concn. and of K can be made with the two-electrode system only when the electrode reactions are reversible, and if the degree of polarisation of the electrodes is either measured, or kept constant by suitable readjustment of the total applied voltage at each measurement. W. J. BAKER

2055. General method of electrochemical titration with the aid of two isometallic polarised micro-electrodes. J. É. Dubois, M. Ashworth and W. Walisch. *Compt. Rend.*, 1956, **242** (11), 1452-1455.—The authors have shown that the abrupt change of potential at the electrodes during a titration carried out in a medium traversed by a limited electrolysis current corresponds with the end-point in standard chemical analysis. The method of "polarised electrodes" has proved entirely successful in reproducing the results of potentiometric or amperometric titrations. It has been used for compleximetric titrations, the determination of lead acetate by oxalic acid and potassium dichromate, and for determining the constituents of a mixture of alkaline halides. It has also been applied to Karl Fischer determinations and to several organic titrations. The advantages claimed for the method include its simplicity and general application, and especially its suitability for low concentrations and for micro-titrations. J. F. P. H. GREENE

2056. Micro-determination of organic compounds, using a new type of relaxational coulometer. I. K. Sykut (Lublin Univ., Poland). *Ann. Univ. M. Curie-Skłodowska, [A]*, 1954, [1956], **9**, 91-122.—An apparatus based on that of Kramer and Fischer (*Anal. Chem.*, 1954, **26**, 415) measures from 0.1 to 10 coulombs (error 0.3 to 0.6%) for currents of 2 to 50 mA. The equipment can also be used for the measurement of high resistances, from 10 to 300 megohms, and of e.m.f. up to 6 V. R. TRUSCOE

See also Abstract 1745.

ABBREVIATIONS

Certain abbreviations in everyday use are not included in the following list. When any doubt might arise from the use of an abbreviation or symbol the word is printed in full.

alternating current	a.c.	milli-equivalent	milli-equiv.
ampere	amp.	milligram	mg
Ångström unit	Å	millilitre	ml
anhydrous	anhyd.	millimetre	mm
approximate, -ly	approx.	millimicrogram	mμg
aqueous	aq.	millimolar	mM
atmospher-e, -ic	atm.	millivolt	mV
boiling-point	b.p.	minute (time)	min.
British thermal unit	B.Th.U.	molar (concentration)	M
calorie (large)	kg-cal.	molecul-e, -ar	mol.
calorie (small)	g-cal.	normal (concentration)	N
centimetre	cm	optical rotation	α _D
coefficient	coeff.	ounce	oz
concentrated	conc.	parts per million	p.p.m.
concentration	concn.	per cent.	%
constant	const.	per cent. (vol. in vol.)	% (v/v)
corrected	(corr.)	per cent. (wt. in vol.)	% (w/v)
crystalline.	} cryst.	per cent. (wt. in wt.)	% (w/w)
crystallised		potential difference	p.d.
cubic	cu.	precipitate (as a noun)	ppt.
current density	c.d.	precipitated	pptd.
cycles per second	c/s	precipitating	pptg.
density	ρ	precipitation	pptn.
density, relative	d or wt. per ml	preparation	prep.
dilute.	dil.	qualitative, -ly	qual.
direct current	d.c.	quantitative, -ly	quant.
distilled	dist.	recrystallised	recryst.
ethylenediaminetetra-acetic acid	EDTA	refractive index	n _D
electromotive force	e.m.f.	relative band speed	R _v
equivalent	equiv.	relative humidity	r.h.
gram	g	revolutions per minute	r.p.m.
gram-molecule	mole	saponification value	sap. val.
half-wave potential	E _{1/2}	saturated calomel electrode	S.C.E.
hour	hr.	second (time)	sec.
hydrogen ion exponent	pH	soluble	sol.
infra-red	i.r.	solution	soln.
insoluble	insol.	specific gravity	sp. gr.
international unit	i.u.	specific rotation	[α] _D
kilogram	kg	square centimetre	sq. cm
kilovolt	kV	standard temp. and pressure	s.t.p.
kilowatt	kW	temperature	temp.
liquid	liq.	ultra-violet	u.v.
maxim-um, -a	max.	vapour density	v.d.
melting-point	m.p.	vapour pressure	v.p.
microgram	μg (not γ)	volt	V
microlitre	μl	volume	vol.
micromole	μmole	watt	W
micron	μ	wavelength	λ
milliampere	mA	weight	wt.

In addition, the following symbols may be used in conjunction with numerical values or in mathematical expressions—

greater than	>	less than	<
not greater than	≥	not less than	≤
is proportional to	∝	of the order of, approximately	≈

The principal Pharmacopoeias are denoted by B.P., U.S.P. or D.A.B., together with the identifying roman numeral or year.

Valency states are represented by a superscript roman numeral, e.g., Fe^{II}, Mo^V. Substances in the ionic state are represented by Na⁺, Fe³⁺, etc., for cations and by Cl⁻, SO₄²⁻, PO₄³⁻, etc., for anions.

ANALYTICAL ABSTRACTS

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